JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

1918.   Vol. CXIV.   Part I.

Abstractors of the *Journal of the Society of Chemical Industry,*
who have contributed to this volume.

J. F. BRIGGS.
T. F. BURTON, B.Sc.
L. A. COLES.
W. F. FREW.
H. J. HODSMAN.
J. H. JOHNSTON.
C. A. KING.

J. H. LANE.
C. A. MITCHELL.
B. NORTH.
A. B. SEARLE.
A. SHONK.
F. C. THOMPSON.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS

ON

PHYSICAL, INORGANIC, MINERALOGICAL,

AND

ANALYTICAL CHEMISTRY.

1918.   Vol. CXIV.   Part II.

Abstractors of the *Journal of the Society of Chemical Industry,*
who have contributed to this volume.

J. F. Briggs.
F. F. Burton, B.Sc.
L. A. Coles.
W. F. Frew.
H. J. Hodsman.
J. H. Johnston.
C. A. King.

J. H. Lane.
C. A. Mitchell.
B. North.
A. B. Searle.
A. Shonk.
F. C. Thompson.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

The following is a list of Journals from which abstracts are made (directly or indirectly) by the Chemical Society and the Society of Chemical Industry. The abbreviated titles printed in italics represent Journals abstracted by the Chemical Society, those printed in roman type being abstracted by the Society of Chemical Industry. Of the former Journals those indicated by an asterisk are also abstracted by the Society of Chemical Industry.

ABBREVIATED TITLE.	JOURNAL.
Abh. Böhm. Akad.	Abhandlungen der Böhmischen Akademie.
Abh. Deut. Naturwiss. Med. Ver. Böhmen.	Abhandlungen der Deutschen Naturwissenschaftlichen und Medizinischen Verein, Böhmen.
Acad. Sci. Fennicae	Acta Societatis Scientiarum Fennicae.
Agric. Bull. F. M. S.	Agricultural Bulletin of the Federated Malay States.
Agric. Exp. Stat. Univ. Wisconsin Res. Bull.	Agricultural Experimental Station, University of Wisconsin, Research Bulletin.
Agric. Gaz. S. Russia	Agricultural Gazette of Southern Russia.
Agric. J. India	Agricultural Journal of India.
Agric. Ledger	Agricultural Ledger.
Agric. Res. Inst., Pusa Rep. (Bull.)	Agricultural Research Institute, Pusa, Report and Bulletins.
Agric. and Sylvic.	Agriculture and Sylviculture (Petrograd).
Allgem. Brau.-Hopf. Zeit.	Allgemeine Brau- und Hopfen-Zeitung.
Allgem. Gerber-Zeit.	Allgemeine Gerber-Zeitung.
Allgem. Z. Bierbrau. u. Malzfabr.	Allgemeine Zeitschrift für Bierbrauerei und Malzfabrikation.
Amat. Fotog.	Amator Fotografen.
Amer. Brewers' J.	American Brewers' Journal.
Amer. Brewers' Rev.	American Brewers' Review.
Amer. J. Bot.	American Journal of Botany.
Amer. J. Dis. Children	American Journal of Diseases of Children.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Publ. Health	American Journal of Public Health.
*Amer. J. Sci.	American Journal of Science.
Amer. Mach.	American Machinist.
Amer. Min.	American Mineralogist.
Amer. Perf.	American Perfumer.
Amer. Phot.	American Photography.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Anal. Soc. Quim. Argentina	Anales de la Sociedad Química Argentina.
Analyst	Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Bot.	Annals of Botany.
Ann. di Bot.	Annali di Botanica.
Ann. Chim.	Annales de Chimie.
Ann. Chim. Analyt.	Annales de Chimie Analytique.
Annali Chim. Appl.	Annali di Chimica Applicata.
Ann. Ecole Agric. Montpellier	Annales de l'Ecole nationale d'Agriculture de Montpellier.
Ann. Falsif.	Annales des Falsifications.
Ann. Geol. Min. Russie	Annuaire de la Géologie et de la Minéralogie de Russie.
Ann. hyg. pub. med. legale.	Annales d'hygiène publique et de médicine légale.
Ann. Inst. Mines, Petrograd	Annales de l'Institut des Mines, Petrograd.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Inst. Polyt., Petrograd	Annales de l'Institut Polytechnique, Petrograd.
Ann. Physik	Annalen der Physik.
Ann. Physique	Annales des Physique.
Ann. R. Staz. Chim. Agrar. Sperim	Annali della R. Stazione Chimico Agraria Sperimentale di Roma.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.

ABBREVIATED TITLE.	JOURNAL.
Ann. Soc. Geol. Belg.: *Publ. rel. au Congo Belge.*	Annales de la Société géologique de Belgique : Publications relatives au Congo Belge.
Apoth. Zeit.	Apotheker-Zeitung.
App. Sci.	Applied Science.
Arb. Gebiet. Physik, Math. Chem.	Arbeiten aus dem Gebiete der Physik, Mathematik und Chemie.
Arb. Gesundh. Amt.	Arbeiten aus dem Gesundheitsamte.
Arch. Anat. Physiol.	Archiv für Anatomie und Physiologie.
Arch. Chem. Mikros.	Archiv Chemie und Mikroskopie.
Arch. Entw.-mech. Org.	Archiv für Entwicklungsmechanik der Organismen.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. farm. sper. sci. aff.	Archivio di farmacologia sperimentale e scienze affini.
Arch. Fisiol.	Archivio di Fisiologia.
Arch. Hyg.	Archiv für Hygiene.
Arch. Int. Med.	The Archives of Internal Medicine.
Arch. ital. Biol.	Archives italiennes de Biologie.
Arch. Med. Pharm. milit.	Archives de Médicine et de Pharmacie militaires.
Arch. Néerland.	Archives Néerlandaises de sciences exactes et naturelles.
Arch. Néerland. physiol.	Archives Néerlandaises de physiologie de l'homme et des animaux.
**Arch. Pharm.*	Archiv der Pharmazie.
Arch. physikal. Chem. Glas. Keram.	Archiv für die physikalische Chemie der Glases und der Keramischen Massen.
Arch. Sci. biol. Petrograd	Archives des Sciences biologiques, Petrograd.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arch. Suikerind. Ned. Indie	Archief voor de Suikerindustrie in Nederlandsch-Indië.
Arkiv. Kem. Min. Geol.	Arkiv. för Kemi, Mineralogi och Geologi.
Arm. Beton	Armierter Beton.
**Atti R. Accad. Lincei*	Atti della Reale Accademia dei Lincei.
Atti R. Accad. Sci. Torino	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Ist. Veneto Sci.	Atti del Istituto Veneto di Scienze, Ettere ed Arti.
Aust. Pharm. Notes	Australian Pharmaceutical Notes and News.
Beitr. Min. Japan	Beiträge zur Mineralogie von Japan.
Berg. Hüttenm. Rundsch.	Berg- und Hüttenmannisches Rundschau.
**Ber.*	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deuts. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
Ber. K. Sächs. Ges. Wiss.	Berichte über die Verhandlungen der Königlich Sächsischen Gesellschaft der Wissenschaften.
Ber. Oberhess. Ges. Natur. Heilkunde.	Berichte der Oberhessischen Gesellschaft für Natur- und Heilkunde zu Giessen.
Ber. Ohara Inst. landw. Forsch.	Berichte des Ohara Instituts für landwirtschaftliche Forschungen.
Berlin. Klin. Woch.	Berliner Klinische Wochenschrift.
**Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationallen Landwirtschafts-Betrieb.
Biochem. Bull.	Biochemical Bulletin.
**Biochem. J.*	Biochemical Journal.
**Biochem. Zeitsch.*	Biochemische Zeitschrift.
Blätter Zucker.	Blätter für Zuckerrübenbau.
Bd. of Trade J.	Board of Trade Journal.
Bol. Acad. Nac. Ciencias, Cordoba.	Boletín de la Academia Nacional des Ciencias, Cordoba.
Boll. Chim. farm.	Bolletino Chimico farmaceutico.
Boll. Soc. Geol. Ital.	Bolletino della Società Geologica Italiana.

ABBREVIATED TITLE.	JOURNAL.
Boll. Soc. Med.-Chirurg.	Bolletino della Società Medico-Chirurgica, Pavia.
Bot. Centr.	Botanisches Centralblatt.
Bot. Gaz.	Botanical Gazette.
Brass. Malt.	Brasserie et Malterie.
Brau- u. Malzind.	Brau- u. Malzindustrie.
Braunkohle	Braunkohle.
Brewers' J.	Brewers' Journal.
Brit. and Col. Pharm.	British and Colonial Pharmacist.
Brit. J. Phot.	British Journal of Photography.
Brit. Med. J.	British Medical Journal.
Buletinul Chim.	Buletinul Chimie.
Bul. Soc. Romane Stiin.	Buletinul Societatii Romane de Stiinte.
Bull. Acad. roy. Belg.	Academie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci. Petrograd.	Bulletin de l'Académie Impériale des Sciences de Petrograd.
Bull. Acad. Sci. Roumaine	Bulletin de la Section Scientifique de l'Académie Roumaine.
Bull. Agric. Intell.	Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association des Chimistes de Sucre et de Distillerie.
Bull. Bureau of Standards (U.S.A.).	Bulletin of the Bureau of Standards (U.S.A.).
Bull. Com. Géol. Finlande.	Bulletin de la Commission Géologique de Finlande.
Bull. Dept. Agric. Ceylon .	Bulletin of the Department of Agriculture, Ceylon.
Bull. Dept. Agric. Trinidad	Bulletin of the Department of Agriculture, Trinidad.
Bull. Forest Exp. Stat. Meguro.	Bulletin of the Forest Experiment Station, Meguro, Tokyo.
Bull. gén. Thérap.	Bulletin général de Thérapeutique médicale, chirurgicale, obstétricale.
Bull. Geol. Inst. Univ. Upsala.	Bulletin of the Geological Institution of the University of Upsala.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Geol. Survey, U.S.A.	Bulletin of the U.S. Geological Survey.
Bull. Geol. Survey, West Australia.	Bulletin of the Geological Survey, West Australia.
Bull. Imp. Centr. Agric. Exp. Stat. Japan.	Bulletin of the Imperial Central Agricultural Experimental Station of Japan.
Bull. Imp. Inst.	Imperial Institute Bulletin.
Bull. Johns Hopkins Hospital	Bulletin of Johns Hopkins Hospital.
Bull. Ranade Indus. Econ. Inst. Poona.	Bulletin of the Ranade Industrial and Economic Institute, Poona.
Bull. School Mines and Met., Univ. Missouri	Bulletin of the School of Mines and Metallurgy, University of Missouri.
Bull. Sci. Pharmacol.	Bulletin des Sciences Pharmacologiques.
*Bull. Soc. chim.	Bulletin de la Société chimique de France.
*Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. chim biol.	Bulletin de la Société de chimie biologique.
Bull. Soc. chim. Maurice	Bulletin de la Société chimique de Maurice.
Bull. Soc. d'Encour.	Bulletin de la Société d'Encouragement pour l'Industrie Nationale.
Bull. Soc. franc. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. Franc. Phot.	Bulletin de la Société Française de Photographie.
Bull. Soc. Ind. Mulhouse	Bulletin de la Société Industrielle de Mulhouse.
Bull. Soc. Ind. Nord.	Bulletin de la Société Industrielle du Nord de la France.
Bull. Soc. Ind. Rouen	Bulletin de la Société Industrielle de Rouen.

ABBREVIATED TITLE.	JOURNAL.
Bull. Soc. Oural. Sci. Nat.	Bulletin de la Société Ouralienne des Amateurs des Sciences Naturelles à Catherineberg.
Bull. Soc. Pharm. Bordeaux	Bulletin des Travaux de la Société de Pharmacie de Bordeaux.
Bull. Wellcome Trop.Res.Lab.	Bulletin of the Wellcome Tropical Research Laboratory.
Cairo Sci. J.	Cairo Scientific Journal.
Canada Dept. Mines Publ..	Canada Department of Mines Publications.
Canadian Med. Assoc. J.	Canadian Medical Association Journal.
Canadian Mining J.	Canadian Mining Journal.
Caoutchouc et Gutta-Percha	Le Caoutchouc et le Gutta-Percha.
Cement	Cement.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Kunstdüngerind.	Centralblatt für Kunstdüngerindustrie.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
Centr. Zuckerind.	Centralblatt für Zuckerindustrie.
Céramique	Céramique.
Ch. of Comm. J.	Chamber of Commerce Journal.
Chemik Polski	Chemik Polski.
Chem. App.	Chemische Apparatur.
Chem. Eng.	Chemical Engineer.
Chem. Erde	Chemie der Erde.
Chem. Ind.	Chemische Industrie.
Chem. News	Chemical News.
Chem. Trade J..	Chemical Trade Journal.
Chem. Umschau Fett-Ind.	Chemische Umschau über die Fett- und Harz-Industrie.
Chem. Weekblad	Chemisch Weekblad.
Chem.-Zeit.	Chemiker-Zeitung.
Chem. Zeitsch.	Chemische Zeitschrift.
Chem. Zentr.	Chemisches Zentralblatt.
Chem. and Drug.	Chemist and Druggist.
Collegium	Collegium.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Academie des Sciences.
Compt. rend. l'Acad. d'Agric.	Comptes rendus des Séances de l'Academie d'Agriculture de France.
Compt. rend. Soc. Biol.	Comptes rendus hebdomadaires de Séances de la Société de Biologie.
Comptes rend. Trav. Lab. Carlsberg	Comptes rendus des Travaux de Laboratoire de Carlsberg.
Dept. Chem. S. Australia, Bull.	Department of Chemistry, South Australia, Bulletins.
Derm. Woch.	Dermatologische Wochenschrift.
Deut. Essigind. .	Deutsche Essigindustrie.
Deut. Mechan. Zeit. .	Deutsche Mechaniker Zeitung.
Deut. med. Woch.	Deutsche medizinische Wochenschrift.
Deut. Parfum. Zeit.	Deutsche Parfumerie Zeitung.
Deuts. Zuckerind.	Deutsche Zuckerindustrie.
Econ. Geol. .	Economic Geology.
Econ. Proc. Roy. Dubl. Soc.	Economic Proceedings of the Royal Dublin Society.
Electrician .	Electrician.
Elektrochem. Zeits.	Elektrochemische Zeitschrift.
Eng. and Min. J.	Engineering and Mining Journal.
Eng. News .	Engineering News.
Eng. Rec. .	Engineering Record.
Engrais	L'Engrais.
Exper. Stat. Rec.	Experimental Station Record.
Fachl. Mitt. Öst. Tabak.	Fachliche Mitteilungen der Österreichische Tabakregie.
Farber-Zeit.	Färber-Zeitung.

Abbreviated Title.	Journal.
Farben-Zeit. . . .	Farben-Zeitung.
Farm	The Farm (Russia).
Fermentforsch. . . .	Fermentforschung.
Ferrum . . .	Ferrum.
Feuerungstechnik . .	Feuerungstechnik.
Flora	Flora.
Földtani Közlöny .	Földtani Közlöny.
Fühlings Landw. Zeit. .	Fühlings Landwirtschaftliche Zeitung.
Gas	Het Gas.
Gas J.	Gas Journal.
Gas Rec.	Gas Record.
Gazzetta	Gazzetta chimica italiana.
Geol. För. Förh. . .	Geologiska Föreningens i Stockholm Förhandlingar.
Geol. Mag. . . .	Geological Magazine.
Gerber	Gerber.
Gesundheitsing . . .	Gesundsheitsingenieur.
Gornosaw. Djelo . .	Gornosawodskoje Djelo.
Gummi-Zeit. . . .	Gummi-Zeitung.
Handl. Vijft. Nat. . .	Handelingen van het Vijftende Natuur.
Hawaii Agric. Exp. Stat. Bull.	Hawaii Agricultural Experiment Station Bulletins.
Heart	Heart.
Helv. Chim. Acta . .	Helvetica Chimica Acta.
Hess. Landw. Zeits. . .	Hessische Landwirthschaftliche Zeitschrift.
Hyg. Rundsch.. . .	Hygienische Rundschau.
Indian Forest Bull. . .	Indian Forest Bulletin.
Indian J. Med. Res .	Indian Journal of Medical Research.
India-rubber J. . .	India-rubber Journal.
Ingenieur	De Ingenieur.
Int. Mitt. Bodenk. . .	Internationale Mitteilungen für Bodenkunde.
Int. Sugar J. . . .	International Sugar Journal.
Int. Z. Metallog. . .	Internationale Zeitschrift für Metallographie.
Int. Zeitsch. phys.-chem. Biol.	Internationale Zeitschrift für physikalisch-chemische Biologie.
Iron Steel Inst. Carnegie Schol. Mem.	Iron and Steel Institute, Carnegie Scholarship Memoirs.
Jahrb. K. K. Geol. Reichsanst	Jahrbuch der K. K. geologischen Reichsanstalt.
Jahrb. Min. . . .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
Jahrb. Min. Beil.-Bd. .	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie, Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
Jahrb. wiss. Bot. . .	Jahrbuch für wissenschaftliche Botanik.
Jahresber. Ges. vaterl. Kultur.	Jahresbericht der schlesischen Gesellschaft für vaterländische Kultur.
Jernk. Ann. . . .	Jern-kontorets Annaler.
J. d'Agric. prat. . .	Journal d'Agriculture Pratique.
J. Agric. Res. . .	Journal of Agricultural Research.
J. Agric. Sci. . .	Journal of Agricultural Science.
J. d'Agric. Trop. . .	Journal d'Agriculture Tropique.
J. Agric. Victoria . .	Journal of Agriculture, Victoria.
* J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Amer. Leather Chem. Assoc.	Journal of the American Leather Chemists' Association.
J. Amer. Med. Assoc. .	Journal of the American Medical Association.
J. Amer. Pharm. Assoc. .	Journal of the American Pharmaceutical Association.
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists.
J. Biol. Chem. . . .	Journal of Biological Chemistry, New York.
J. Board Agric. . . .	Journal of the Board of Agriculture.

ABBREVIATED TITLE.	JOURNAL.
J. Canad. Min. Inst. . .	Journal of the Canadian Mining Institute.
J. Chem. Ind. Tokyo . .	*See* Kōgyō- Kwagaku-Zasshi.
J. Chem. Met. Soc. S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa.
J. Chim. physique . .	Journal de Chimie physique.
J. Coll. Agric. Sapporo .	Journal of the College of Agriculture, Sapporo, Japan.
J. Coll. Agric. Tohoku .	Journal of the College of Agriculture, Tohoku Imperial University, Japan.
J. Coll. Agric. Tokyo . .	Journal of the College of Agriculture, Tokyo Imperial University, Japan.
J. Coll. Eng. Univ. Tokyo	Journal of the College of Engineering, University of Tokyo.
J. Coll. Sci. Tokyo . .	Journal of the College of Science, Imperial University of Tokyo.
J. Exp. Med. . . .	Journal of Experimental Medicine.
J. Franklin Inst. . .	Journal of the Franklin Institute.
J. Gasbeleucht. . . .	Journal für Gasbeleuchtung und Wasserversorgung.
J. Genetics	Journal of Genetics.
J. Geol.	Journal of Geology.
J. Geol. Soc. Tokyo . .	Chishitsugaku Zasshi (Journal of the Geological Society of Tokyo).
J. Hygiene	Journal of Hygiene.
J. Imp. Gas Assoc. Tokyo	Journal of the Imperial Gas Association of Tokyo.
J. Ind. Eng. Chem. . .	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing . .	Journal of the Institute of Brewing.
J. Inst. Petroleum Tech. .	Journal of the Institute of Petroleum Technologists.
J. Inst. Sanit. Eng. . .	Journal of the Institute of Sanitary Engineers.
J. Landw.	Journal für Landwirtschaft.
J. Manchester School Tech.	Journal of the Manchester School of Technology.
J. Marine Biol. Assoc. U.K.	Journal of the Marine Biological Association of the United Kingdom.
J. Med. Res. . . .	Journal of Medical Research.
J. Path. Bact. . . .	Journal of Pathology and Bacteriology.
J. Pharm. Chim. . .	Journal de Pharmacie et de Chimie.
J. Pharm. Expt. Ther. .	Journal of Pharmacology and Experimental Therapeutics.
J. Physical Chem. . .	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. Physiol. Path. gén. . .	Journal de Physiologie et de Pathologie générale.
J. pr. Chem. . . .	Journal für praktische Chemie.
J. Proc. Asiatic Soc. Bengal.	Journal and Proceedings of the Asiatic Society of Bengal.
J. Roy. Agric. Soc. . .	Journal of the Royal Agricultural Society.
J. Roy. Army Med. Corps .	Journal of the Royal Army Medical Corps.
J. Roy. Hort. Soc. . .	Journal of the Royal Horticultural Society.
J. Roy. Soc. New South Wales.	Journal and Proceedings of the Royal Society of New South Wales.
J. Roy. Soc. West Australia	Journal of the Royal Society of West Australia.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Scot. Met. Soc. . .	Journal of the Scottish Meteorological Society.
J. Soc. Arts . . .	Journal of the Royal Society of Arts.
J. Soc. Dyers and Col. .	Journal of the Society of Dyers and Colourists.
J. Soc. Russe Métall. . .	Journal de la Société Russe de Métallurgie.
J. S. African Assoc. Anal. Chem.	Journal of the South African Association of Analytical Chemists.
J. Textile Inst. . . .	Journal of the Textile Institute.
J. Usines Gaz . . .	Journal des Usines à Gaz.
J. Washington Acad. Sci. .	Journal of the Washington Academy of Science.
J. West Scotland Iron Steel Inst.	Journal of the West of Scotland Iron and Steel Institute.

ABBREVIATED TITLE.	JOURNAL.
K. Svenska Vet.-Akad. Handl.	Kongliga Svenska Vetenskaps Akademiens Handlingar.
Kali	Kali.
Karbid u. Azet. . . .	Karbid und Azetylen.
Kentucky Exp. Stat. Bull.	Kentucky Experimental Station, Bulletin.
Keram. Rundsch. . .	Keramisch Rundschau.
Kew Bull. . . .	Kew Bulletin.
Kiserlet Közl. . . .	Kiserlet Közlémények.
Klein u. Mittelbrauer . .	Klein und Mittelbrauer.
Kongl. Landtbr. Handl. Tidskr.	*See* Bull. Agric. Intell.
Kōgyō-Kwagaku-Zasshi (J. Chem. Ind. Japan).	Kōgyō-Kwagaku-Zasshi (Journal of Chemical Industry, Japan).
*Kolloid Zeitsch. . .	Kolloid Zeitschrift.
*Koll. Chem. Beihefte .	Kolloid-chemische Beihefte.
Kosmos	Kosmos (Lemberg).
Kühn-Archiv . . .	Kühn-Archiv.
Kunststoffe . . .	Kunststoffe.
Lancet	The Lancet.
Landw. Jahrb. . . .	Landwirtschaftliche Jahrbücher.
Landw. Versuchs.-Stat. .	Die landwirtschaftlichen Versuchs-Stationen.
Leather Trades Rev. . .	Leather Trades Review.
Leather Trades Year Boo .	Leather Trades Year Book.
Leather World . .	Leather World.
Ledertech. Rundsch. . .	Ledertechnische Rundschau.
Leipzig. Monatsch. Textil-Ind.	Leipziger Monatschrift für Textil-Industrie.
Le Radium . . .	Le Radium.
L'Ind. Chimica . . .	L'Industria Chimica.
L'Ind. Chimique . . .	L'Industrie Chimique.
Lilly Sci. Bull. . . .	Lilly Scientific Bulletin.
Local Govt. Bd. Reports .	Local Government Board Reports.
Louisiana Bull. . . .	Louisiana Bulletin.
Louisana Planter . .	Louisiana Planter.
Lunds. Univ. Arsskr. . .	Lunds Universitets Ârs-skrift.
Math. és Termés. Ért. .	Mathematikai és Természettudományi Értesitö, Budapest.
Mat. Grasses . . .	Les Matières Grasses.
Medd. K. Vetenskapsakad. Nobel-Inst.	Meddelanden frân Kongl-Vetenskapsakademiens Nobel-Institut.
Medd. on Grönland . .	Meddelser on Grönland.
Med. Chron. . . .	Medical Chronicle.
Med. Klinik . . .	Medizinesche Klinik.
Mem. Acad. Sci. Petrograd .	Mémoires de l'Académie Impériale des Sciences de Petrograd.
Mem. Accad. Lincei . .	Memorie della Reale Accademia dei Lincei.
Mem. Accad. Sci. Torino .	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Kyōtō .	Memoirs of the College of Science, Kyōtō Imperial University.
Mem. Coll. Sci. and Eng. Kyōtō Imp. Univ.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Dept. Agric. India .	Memoirs of the Department of Agriculture in India.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Mém. Poudres et Salpêtres .	Mémoriale des Poudres et Salpêtres.
Mem. Soc. Ing. Civ. . .	Mémoires de la Société des Ingénieurs Civils de France
Mem. Soc. Natur. Kiev .	Mémoires de la Société des Naturalistes de Kiev.
Mem. Soc. Toscana Sci. Nat.	Memorie della Società Toscana di Scienze naturali residente in Pisa.
Metall u. Erz . . .	Metall und Erz.

ABBREVIATED TITLE.	JOURNAL.
Met. and Chem. Eng.	Metallurgical and Chemical Engineering.
Metallurgie	Metallurgie.
Metrop. Water Bd. Rep.	Metropolitan Water Board Reports.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Min. and Eng. Rev.	Mining and Engineering Review.
Ministry of Agric. Egypt. Tech. Sci. Service	Ministry of Agriculture of Egypt. Technical Science Service.
Mitt. Centralst. wiss.-techn. Unters.	Mittheilungen aus der Centralstelle für wissenschaftlich-technische Untersuchungen.
Mitt. deut. Landw.-Ges.	Mittheilungen der deutschen Landwirthschafts-Gesellschaft.
Mitt. deut. milchwirt. Ver.	Mitteilungen des deutschen milchwirtschaftlichen Vereins.
Mitt. geol. Landesanst.	Mittheilungen der geologischen Landesanstalt von Elsass-Lothringen.
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West.
Mitt. k. k. Techn. Versuchsamtes	Mittheilungen des k. k. Technischen Versuchsamtes.
Mitt. med. Ges. Tokyo	Mittheilungen der medizinischen Gesellschaft zu Tokyo.
Mitt. Naturforsch. Ges. Halle.	Mittheilungen der Naturforschenden Gesellschaft zu Halle.
Molk.-Zeit.	Molkerei-Zeitung.
Monatsh.	Monatshefte für Chemie und verwandte Teile anderer Wissenschaften.
Monatsh. Math. Physik	Monatshefte für Mathematik und Physik.
Mon. Sci.	Moniteur Scientifique.
Montan. Rundsch.	Montanische Rundschau.
Month. Not. Roy. Astr. Soc.	Monthly Notices of the Royal Astronomical Society, London.
Münch. med. Woch.	Münchener medizinische Wochenschrift.
Mycol. Zentr.	Mycologisches Zentralblatt.
Nachr. Ges. Wiss. Göttingen.	Nachrichten von der Königlichen Gesellschaft der Wissenschaften zu Göttingen.
Nature	Nature.
Naturwiss.	Die Naturwissenschaften.
Naturw. Rdsch.	Naturwissenschaftliche Rundschau.
Nephthanoje Djelo	Nephthanoje Djelo.
New York Agr. Expt. Sta. Bull.	New York Agricultural Experiment Station Bulletins.
New Zealand Dominion Laby. Rept.	New Zealand Dominion Laboratory Reports.
Nova Acta Soc. Sci.	Nova Acta Regiae Societatis Scientiarum Upsaliensis.
Nuovo Cim.	Il Nuovo Cimento.
Öfvers. Finska Vet.-Soc.	Öfversigt af Finska Vetenskaps-Societetens Förhandlingar, Helsingfors.
Oelmotor	Der Oelmotor.
Oesterr. Chem.-Zeit.	Oesterreichische Chemiker-Zeitung.
Oesterr. Z. Berg- u. Hüttenw.	Oesterreichische Zeitschrift für Berg- und Hüttenwesen.
Oil and Colour Trades J.	Oil and Colour Trades Journal.
Oil, Paint, and Drug Rep.	Oil, Paint, and Drug Reporter.
Oversigt Danske Vid. Selsk.	Oversigt over det Kongelige Danske Videnskabernes Selskab Forhandlingar.
Pahasapa Quart.	Pahasapa Quarterly.
Paper	Paper.
Paper Maker	Paper Maker.
Paper Making	Paper Making.

ABBREVIATED TITLE.	JOURNAL.
Papierfabr.	Papier-Fabrikant.
Papier-Zeit.	Papier-Zeitung.
Perf. and Essent. Oil Rec.	Perfumery and Essential Oil Record.
Per. spis. Sofia	Periodicesko spisanie Sofia.
Petroleum.	Petroleum.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Post.	Pharmazeutische Post.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Pharmazevt. J.	Pharmazevtizeski Journal.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Philippine J. Sci.	Philippine Journal of Science.
Phot. Ind.	Photographische Industrie.
Phot. J.	Photographic Journal.
Phot. Korr.	Photographische Korrespondenz.
Phot. Rundsch.	Photographische Rundschau.
Physical Rev.	Physical Review.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Porto Rico Exper. Stat. Bull.	Porto Rico Experiment Station Bulletin.
Proc. Amer. Phil. Soc.	Proceedings of the American Philosophical Society.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Amer. Soc. Biol. Chem.	Proceedings of the American Society of Biological Chemists.
Proc. Amer. Soc. Civ. Eng.	Proceedings of the American Society of Civil Engineers.
Proc. Amer. Soc. Testing Materials	Proceedings of American Society for Testing Materials.
Proc. Amer. Wood Preservers' Assoc.	Proceedings of American Wood Preservers' Association.
Proc. Austral. Inst. Min. Eng.	Proceedings of the Australasian Institute of Mining Engineers.
Proc. Brit. Foundrymen's Assoc.	Proceedings of British Foundrymen's Association.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. Durham Phil. Soc.	Proceedings of the Durham Philosophical Society.
Proc. Eng. Soc. W. Pa.	Proceedings of the Engineers' Society of Western Pennsylvania.
Proc. Inst. Civ. Eng.	Proceedings of the Institution of Civil Engineers.
Proc. Inst. Mech. Eng.	Proceedings of the Institution of Mechanical Engineers.
Proc. Inst. Min. and Met.	Proceedings of the Institution of Mining and Metallurgy.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Nat. Acad. Sci.	Proceedings of the National Academy of Sciences.
Proc. Nova Scotia Inst. Sci.	Proceedings of the Nova Scotia Institute of Science.
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physical Soc. London.	Proceedings of the Physical Society of London.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Inst.	Proceedings of the Royal Institution of Great Britain.
Proc. Roy. Irish Acad.	Proceedings of the Royal Irish Academy.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Proc. Roy. Soc. Med.	Proceedings of the Royal Society of Medicine.
Proc. Roy. Soc. Queensland.	Proceedings of the Royal Society of Queensland.

ABBREVIATED TITLE.	JOURNAL.
Proc. Roy. Soc. Tasmania .	Proceedings of the Royal Society of Tasmania.
Proc. Soc. Chem. Ind. Victoria.	Proceedings of the Society of Chemical Industry, Victoria.
Proc. Soc. Exp. Biol. Med. .	Proceedings of the Society for Experimental Biology and Medicine.
Proc. U.S. Nat. Mus. . .	Proceedings of the United States National Museum.
Proc. verb. Soc. Toscana Sci. Nat.	Processi verbali Società Toscana di Scienze Naturali.
Quart. J. Exp. Physiol. .	Quarterly Journal of Experimental Physiology.
Quart. J. Geol. Soc. . .	Quarterly Journal of the Geological Society.
Quart. J. Med. . . .	Quarterly Journal of Medicine.
Queensland Agric. J. . .	Queensland Agricultural Journal.
Radium in Biol. Heilkunde	Radium in Biologie und Heilkunde.
Rec. Australian Mus. .	Records of the Australian Museum.
Rec. trav. bot. Néerland. .	Recueil des travaux botaniques Néerlandaises.
*Rec. trav. chim. . .	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche, Napoli.
Rend. Ist. Lomb. Sci. Lett. .	Rendiconti dell' Istituto Lombardo di Scienze e Lettere.
Rend. Soc. Chim. Ital. .	Rendiconto della Società Chimica Italiana.
Rep. Aust. Assoc. Sci. .	Report of the Australian Association for the Advancement of Science.
Rep. Brit. Assoc. . .	Report of the British Association for the Advancement of Science.
Rep. Pharm. . . .	Repertoire de Pharmacie.
Rev. Viticolt . . .	Revista Viticolt.
Rev. gén. Bot. . .	Revue générale de Botanique.
Rev. gén. Chim. pure appl.	Revue générale de Chimie pure et appliquée.
Rev. Gén. Mat. Col. . .	Revue Générale des Matières Colorantes.
Rev. Mét.	Revue de Métallurgie.
Rev. Real Acad. Ciencias exact. Madrid.	Revista de la Real Academia de Ciencias exactas, Fisicas y Naturales de Madrid.
Riv. Min. Crist. Ital. .	Rivista di Mineralogia e Cristallografia Italiana.
Russian Mining J. . .	Russian Mining Journal.
Sbornik Klubu Pri. .	Sbornik Klubu Prirodovedeckeho (Prague).
Schimmel's Rep. . .	Schimmel's Reports.
Schweiz. Apoth. Zeit. .	Schweizerische Apotheker Zeitung.
Schweiz. Woch. Chem. Pharm.	Schweizerische Wochenschrift für Chemie und Pharmacie.
Science	Science.
Scient. Amer. . . .	Scientific American.
*Sci. Ind. Rep. Roure-Bertrand Fils.	Scientific and Industrial Reports of Roure-Bertrand Fils.
Sci. Proc. Roy. Dubl. Soc. .	Scientific Proceedings of the Royal Dublin Society.
Sci. Rep. Tohoku Imp. Univ.	Science Reports, Tohoku Imperial University.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Seifenfabr.	Der Seifenfabrikant.
Seifensied. Zeit. . .	Seifensieder Zeitung.
Selsk. Khoz. Les. Petrograd	Selskoie Khoziaistvo i Lesovodstvo Petrograd.
Shoe and Leather Rep. .	Shoe and Leather Reporter.
Silikat-Zeits. . . .	Silikat-Zeitschrift.
Sitzungsber. Ges. Naturwiss. Marburg.	Sitzungsberichte der Gesellschaft zur Beförderung der gesammten Naturwissenschaften in Marburg.
Sitzungsber. Heidelberger Akad. Wis.	Sitzungsberichte der Heidelberger Akademie der Wissenschaften.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der Königlich bayerischen Akademie der Wissenschaften zu München.

ABBREVIATED TITLE.	JOURNAL.
Sitzungsber. K. Akad. Wiss. Wien.	Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften, Wien.
Sitzungsber. Med. Naturwiss. Ges. Münster.	Sitzungsberichte der Medizinisch-Naturwissenschaftlichen Gesellschaft zu Münster-in-Westfalens.
Sitzungsber. Naturforsch. Ges. Petrograd.	Sitzungsberichte der Naturforschenden Gesellschaft zu Petrograd.
Sitzungsber. Naturforsch. Ges. Rostock.	Sitzungsberichte der Naturforschenden Gesellschaft zu Rostock.
Sitzungsber. phys. med. Ges. Erlangen.	Sitzungsberichte der physikalisch-medizinischen Gesellschaft zu Erlangen.
Skand. Arch. Physiol.	Skandinavisches Archiv für Physiologie.
Smithsonian Miscell. Coll.	Smithsonian Miscellaneous Collections.
Soil Sci.	Soil Science.
South African J. Sci.	South African Journal of Science.
Spezialmonats. Brau- Malz.	Spezialmonatshefte für Brau- und Malzerei betriebskontrolle.
Sprechsaal.	Sprechsaal.
Stahl u. Eisen	Stahl und Eisen.
Staz. sper. agr. ital.	Stazioni sperimentali agrarie italiane.
Strahlenther.	Strahlentherapie.
Sucr. Indig.	Sucrerie Indigène.
Süddeut. Apoth. Zeit.	Süddeutsche Apotheker Zeitung.
Suikerind.	De Suikerindustrie.
Suom. Tied. Toim.	Suomalaisen Tiedeakatemian Toimituskia.
Svensk Kem. Tidskr.	Svenska Kemisk Tidskrift.
T.	Transactions of the Chemical Society.
Teknikern	Teknikern.
Tekn. Tidsk.	Teknisk Tidskrift.
Textile Col.	Textile Colourist.
Ther. Gegenw.	Die Therapie der Gegenwart.
Ther. Monatsh.	Therapeutische Monatshefte.
Tidsk. Kemi, Farm., Ter.	Tidskrift Kemi, Farm. og Terape.
Tidsk. Teknikern.	Tidskriften Teknikern.
Times Eng. Supplt.	Times Engineering Supplement.
Tonind.-Zeit.	Tonindustrie-Zeitung.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Amer. Foundrymen's Assoc.	Transactions of the American Foundrymen's Association.
Trans. Amer. Inst. Chem. Eng.	Transactions of the American Institute of Chemical Engineers.
Trans. Amer. Inst. Metals	Transactions of the American Institution of Metals.
Trans. Amer. Inst. Min. Eng.	Transactions of the American Institute of Mining Engineers.
Trans. Engl. Ceram. Soc.	Transactions of the English Ceramic Society.
* Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Inst. Metals	Transactions of the Institute of Metals.
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute.
Tr. N. Eng. Inst. Min. and Met.	Transactions of the North of England Institute of Mining and Metallurgy.
Trans. New Zealand Inst.	Transactions of the New Zealand Institute.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Surveyors' Inst.	Transactions of the Surveyors' Institute.
Trav. Mus. Geol. Acad. Sci. Petrograd.	Travaux de Musee Geologique près l'Academie Impériale des Sciences de Petrograd.

ABBREVIATED TITLE.	JOURNAL.
Trav. Soc. Natur. Petrograd.	Travaux de la Société Impériale des Naturalistes de Petrograd.
Tropenpflanzer . . .	Tropenpflanzer.
Tsch. Min. Mitt. . .	Tschermak's Mineralogische Mitteilungen.
U.S. Bureau of Mines, Bull. and Tech. Papers.	United States Bureau of Mines, Bulletins and Technical Papers.
U.S. Bureau Plant Ind. .	United States Bureau of Plant Industry.
U.S. Comm. Rept. . .	United States Commerce Reports, Daily Consular and Trade Reports.
U.S. Dept. Agric. Bull. .	United States Department of Agriculture Bulletins.
U.S. Hyg. Labor. Bull. .	United States Hygienic Laboratory Bulletins.
Univ. Illinois Bull. . .	University of Illinois Bulletins.
Utah Agric. Coll. Exper. Stat. Bull.	Utah Agricultural College Experiment Station Bulletins.
Ver. deut Textilver. . .	Verein deutscher Textilveredlungsindustrie.
Verh. Geol. Reichsanst. Wien.	Verhandlungen der k. k. geologischen Reichsanstalt in Wien.
Verh. Ges. deut. Naturforsch. Aertze.	Verhandlung der Gesellschaft deutscher Naturforscher und Aertze.
Verh. Naturhist. med. Ver. Heidelberg.	Verhandlungen des naturhistorisch-medizinischen Vereins zu Heidelberg.
Verh. Naturhist. Rheinl. .	Verhandlungen des naturhistorischen Vereins der preussischen Rheinlande und Westfalens.
Verh. Physiol. Ges. Berlin .	Verhandlungen der Physiologischen Gesellschaft zu Berlin.
Verh. Schweiz. Nat. Ges. .	Verhandlungen der Schweizerischen Naturforschenden Gesellschaft, Basel.
Verslag Landb. . . .	Verslag Landbouwkund Onderzoek Ryklandbouwproefstat.
Vet. Rec. . . .	Veterinary Record.
Vict. Mem. Mus. Geol. Survey, Canada.	Victoria Memorial Museum Geological Survey of Canada, Bulletin
Videnskab. Skrifter . .	Skrifter udgivne af Videnskabsselskabet i Kristiania.
Wasser u. Gas . . .	Wasser und Gas.
West Ind. Agric. News .	West Indian Agricultural News.
West Ind. Bull. . . .	West Indian Bulletin.
Westnik Sacch. Prom. .	Westnik Saccharnoi Promyschlenosti.
Wiener Klin. Woch. . .	Wiener Klinische Wochenschrift.
Wiss. Abhandl. Physikal-Tech. Reichsanst.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Wochbl. Papierfabr. . .	Wochenblatt für Papierfabrikation.
Woch. f. Brau. . . .	Wochenschrift für Brauerei.
Yakugakuzashi . . .	Yakugakuzashi.
Zeitsch. allg. Physiol. .	Zeitschrift für allgemeine Physiologie.
Zeitsch. anal. Chem. .	Zeitschrift für analytische Chemie.
Z. angew. Chem. . .	Zeitschrift für angewandte Chemie.
Zeitsch anorg. Chem. .	Zeitschrift für anorganische und allgemeine Chemie.
Zeitsch. Biol. . . .	Zeitschrift für Biologie.
Zeitsch. deut. Geol. Ges. .	Zeitschrift der deutschen Geologischen Gesellschaft.
Zeitsch. Elektrochem. .	Zeitschrift für Elektrochemie.
Zeitsch. exp. Path. Ther. .	Zeitschrift für experimentelle Pathologie und Therapie.
Z. Farben-Ind. . .	Zeitschrift für Farben-Industrie.
Z. Forst- u. Jagdwesen .	Zeitschrift für Forst- und Jagdwesen.
Z. Gärungsphysiol. . .	Zeitschrift für Gärungsphysiologie.
Z. ges. Brauw. . . .	Zeitschrift für das gesammte Brauwesen.
Zeitsch. ges. exp. Med. .	Zeitschrift für die gesamte experimentelle Medizin.
Z. ges. Getreidew. . .	Zeitschrift für das gesamte Getreidewesen.
Z. ges. Schiess- u. Sprengstoffw.	Zeitschrift für das gesammte Schiess- und Sprengstoffwesen.
Zeitsch Hyg. . . .	Zeitschrift für Hygiene und Infektionskrankheiten.

ABBREVIATED TITLE.	JOURNAL.
Zeitsch. Immunit. . .	Zeitschrift für Immunitätsforschung und experimentelle Therapie.
Zeitsch. Instrument. . .	Zeitschrift für Instrumentenkunde.
Z. Kali . . .	Zeitschrift für Kali.
Zeitsch. Kryst. Min. . .	Zeitschrift für Krystallographie und Mineralogie.
Z. landw. Versuchsw. Oesterr.	Zeitschrift für das landwirtschaftlichen Versuchswesen in Oesterreich.
Z. öffentl. Chem. . .	Zeitschrift für öffentliche Chemie.
*Zeitsch. physikal. Chem. .	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandschaftslehre.
Zeitsch. physikal. Chem. Unterr.	Zeitschrift für den physikalischen und Chemischen Unterricht.
Zeitsch. physiol. Chem. .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol. . .	Zeitschrift für praktische Geologie.
Z. Spiritusind. . . .	Zeitschrift für Spiritusindustrie.
Z. Unters. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Z. Ver. deut. Zuckerind. .	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Mikrosk. .	Zeitschrift für wissenschaftliche Mikroskopie und mikroskopische Technik.
*Zeitsch. wiss. Photochem. .	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Z. Zuckerind. Böhm. . .	Zeitschrift für Zuckerindustrie in Böhmen.

JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

The Use of Metal-ammoniums in Organic Chemistry.
E. CHABLAY (*Ann. Chim.*, 1917, [ix], **8**, 145—220).—A résumé of
work already published (compare A., 1905, i, 502; 1906, i, 722;
1907, i, 53; 1911, i, 939; 1912, i, 3, 244, 528; 1913, i, 438).
W. G.

**The Method of Pyrogenic Decomposition of Methyl
Alcohol at High Temperatures.** (MLLE.) EGLANTINE PEYTRAL
(*Compt. rend.*, 1917, **165**, 703—705).—From determinations of
the relative amounts of carbon monoxide and formaldehyde
obtained when methyl alcohol vapour is passed at different rates
through a platinum tube at 1150°, it is shown that the decomposi-
tion takes place in two stages which proceed simultaneously. In
the first stage, formaldehyde and hydrogen are formed, and the
formaldehyde is then decomposed, giving carbon monoxide and
hydrogen. W. G.

**A Hydrate of a Salt Precipitated by Warming its Aqueous
Solution.** D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **100**,
355—356).—Barium ethyl phosphate, $BaC_2H_5PO_4$, is prepared by
warming together on the water-bath for some hours a mixture of
ethyl metaphosphate, $C_2H_5PO_3$, and methyl alcohol, and sub-
sequently neutralising with barium hydroxide. When the aqueous
solution of the barium salt is warmed, crystals separate, which re-

dissolve on cooling. The crystals seem to be a hydrated form of barium ethyl phosphate. They can also be precipitated from aqueous solution by means of alcohol.   E. H. R.

The Preparation and Hydrolysis of Esters derived from the Substituted Aliphatic Alcohols. W. A. DRUSHEL and G. R. BANCROFT (*Amer. J. Sci.*, 1917, [iv], **44**, 371—380).—A description of experiments on the rate of hydrolysis of the acetates derived from ethyl, β-hydroxyethyl, β-methoxyethyl, α- and β-ethoxyethyl, α- and β-chloroethyl, and β-bromoethyl alcohols by aqueous $N/10$-hydrochloric acid.

β-Hydroxyethyl acetate, b. p. 187—189°, was obtained by digesting equimolecular proportions of ethylene glycol and acetic acid for eight hours over anhydrous copper sulphate (2 mols.); attempts to prepare β-hydroxyethyl acetate by reaction with anhydrous potassium acetate and alcoholic ethylene bromide yielded only glycol diacetate. The β-ethoxyethyl alcohol necessary for the production of the corresponding acetate was formed by digesting equimolecular quantities of β-bromoethyl acetate and sodium ethoxide for half an hour in alcoholic solution.

With a halogen atom or alkyloxy-group attached to the α-carbon atom of an ethyl ester, the rate of hydrolysis is too rapid to be measured in the ordinary way; α-chloroethyl acetate, α-chloroethyl propionate, and α-ethoxyethyl acetate undergo almost instantaneous hydrolysis in $N/10$-hydrochloric acid, yielding the corresponding fatty acid, together with a mixture of acetaldehyde and hydrogen chloride in the first two cases and of acetaldehyde and ethyl alcohol in the case of the third ester.

The β-substituted acetates at 25° to 45° undergo hydrolysis less rapidly than ethyl acetate, the hydroxyl and alkyloxyl groups and the halogens producing approximately the same degree of retardation; the ethoxyl radicle produces a slightly greater effect than the methoxyl radicle, whilst bromine is of somewhat less influence than chlorine. The temperature-coefficients for the β-substituted esters range from 2·2 to 2·5 for 10°, the values of the coefficient for the β-bromoethyl acetate being slightly lower than for the other esters. In the case of the β-substituted esters, the hydrolysis follows a normal course, although the β-halogen compounds at the higher temperatures tend to form small quantities of hydrogen chloride or bromide.   D. F. T.

☞ **Selenium Dioxide–Oxalic Acid, its Preparation and Theoretical Significance.** TH. GASSMANN (*Zeitsch. physiol. Chem.*, 1917, **100**, 209—214).—Two grams of selenium dioxide are dissolved in concentrated hydrochloric acid and the solution evaporated almost to dryness on the water-bath. The residue is moistened with dilute hydrochloric acid and then 25 c.c. of a 33% solution of potassium oxalate are added. After mixing, a white, flaky precipitate gradually forms, which is collected and dried. *Selenium dioxide–oxalic acid*, $SeO_2(C_2H_2O_4)_2$, is thus

obtained as a white powder, which turns brown on heating at 90°
or exposure to light. The elementary composition of the material
is not thereby altered, which suggests that the alteration in colour
is due to an intramolecular change. The author considers that
in the new compound the four carboxyl radicles are combined
directly with the selenium atom, which thereby becomes octavalent,
$SeO_2(CO_2H)_4$. It is also suggested that the selenium found in
bones and teeth (Gassmann, A., 1916, i, 772) is present in the
form of a compound analogous in structure to selenium dioxide–
oxalic acid. H. W. B.

**Pasteur's Principle of the Relation between Molecular
and Physical Asymmetry. IV. Racemic and Optically
Active Complex Salts of Rhodium Trioxalic Acid.** F. M.
JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**,
263—279. Compare A., 1915, i, 867; ii, 399; this vol., i, 7).—
Complex compounds of the type $[MeX''_3]Y_n$ should, accord-
ing to Werner's theory, have a molecular structure the con-
figuration of which exhibits asymmetry of the trigonal trapezo-
hedral class. Failure to detect enantiomorphism in the crystals
of the optically active substances in triethylenediamine compounds
of this type is to be attributed to the chemical identity of the
radicles around the central atom. In cases where these radicles
contain oxygen, however, the expected hemihedrism is found. The
d- and *l*-potassium rhodium oxalates, which have now been ex-
amined, form right- and left-handed crystals of the expected type
of symmetry. Werner's claim to have resolved the racemic com-
pound by spontaneous crystallisation cannot be substantiated.
Indeed, from physico-chemical considerations, it is impossible,
since the *d*- and *l*-compounds are more soluble than the *r*-salt.
Werner's supposed hemihedral crystals were probably distorted
trigonal crystals of the racemic compound. The optical rotation
of the active compounds is specially interesting, for solutions of
the *d*-compound are inactive for light of wave-length 5970
Ångström units, dextrorotatory for smaller, and lævorotatory for
greater wave-lengths. At wave-length 5970, the optical antipodes
are indistinguishable from the racemic compound. For this wave-
length there is no trace of an absorption line, and the idea of a
connexion between abnormal rotation dispersion and selective
absorption must be given up.

r-Potassium rhodium oxalate, $K_3[Rh(C_2O_4)_3],4\frac{1}{2}H_2O$, garnet-red,
transparent plates, triclinic [$a:b:c=1.0732:1:1.0316$; $\alpha=98°10\frac{2}{3}'$;
$\beta=104°17\frac{1}{3}'$; $\gamma=66°11\frac{2}{3}'$].

d- and *l*-Potassium rhodium oxalate $(+H_2O)$ form blood-red,
massive crystals of varying habit belonging to the trigonal trapezo-
hedral class [$a:c=1:0.8938$; $\alpha=100°38'$]. The hemihedral
character of the crystals is shown by the occurrence of the trigonal
bipyramid $\{22\bar{4}1\}$ and $\{2241\}$ on the *d*- and *l*-crystals respectively.

The silver rhodium oxalate, $[Rh(C_2O_4)_3]Ag_3$, has been prepared
in long, red needles, and from it, by interchange with triethylene-

diaminerhodium halogenides, nine possible racemic and active isomerides of the complex compound, $[Rh(C_2H_8N_2)_3][Rh(C_2O_4)_3]$.

r-Potassium rhodium malonate, $[Rh(C_3H_2O_4)_3]K_3,3H_2O$, forms orange-red, monoclinic plates $[a:b:c = 1\cdot 2309:1:1\cdot 0783$; $\beta = 86°36']$.

r-Potassium iridium oxalate ($+4\frac{1}{2}H_2O$) is isomorphous with the corresponding rhodium salt. It forms beautiful, lustrous orange crystals, triclinic $[a:b:c = 1\cdot 0771:1:1\cdot 0405$; $\alpha = 98°38\frac{1}{2}'$; $\beta = 104°3'$; $\gamma = 66°9\frac{1}{2}']$.   E. H. R.

Complex Salts of Ferrimalonic Acid. F. M. JAEGER and R. T. A. MEES (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 283—291).

—The strychnine and brucine salts of ferrimalonic acid crystallise in small, greenish-yellow crystals, but after fractionation and elimination of the alkaloid, only optically inactive solutions were obtained. The tristrychnine salt (str = strychnine), $[Fe(C_3H_2O_4)_3]str_3,6H_2O$, showed a rotation corresponding approximately with the alkaloid present, and no active potassium salt was obtained. The ferrioxalates could not be resolved by means of their diammonium-strychnine, -quinine, -cinchonine, or -morphine salts, or by means of the corresponding hydrazine salts. The following racemic salts have been prepared and examined crystallographically. There appear to be three series of hydrated salts of the alkali metals, rhombic and triclinic salts with $1H_2O$ and triclinic salts with $4H_2O$.

Potassium ferrimalonate, $K_3[Fe(C_3H_2O_4)_3],4H_2O$, large, transparent, emerald-green triclinic crystals $[a:b:c = 0\cdot 4924:1:0\cdot 4897$; $\alpha = 98°5'$; $\beta = 104°30'$; $\gamma = 82°52\frac{1}{2}']$.

Ammonium ferrimalonate, $(NH_4)_3[Fe(C_3H_2O_4)_3],H_2O$, pale green, dichroic plates, rhombic bipyramidal $[a:b:c = 0\cdot 9407:1:0\cdot 6860]$.

Rubidium ferrimalonate, $Rb_3[Fe(C_3H_2O_4)_3],H_2O$, isomorphous with the last $[a:b:c = 0\cdot 9442:1:0\cdot 6985]$. A triclinic monohydrate was also observed, but could not be measured.

Cæsium ferrimalonate, $Cs_3[Fe(C_3H_2O_4)_3],H_2O$, isomorphous with the rhombic rubidium salt $[a:b:c = 0\cdot 9548:1:0\cdot 7089]$.

Thallous ferrimalonate, $Tl_3[Fe(C_3H_2O_4)_3],H_2O$, rhombic, well-developed, flat plates, isomorphous with the last $[a:b:c = 0\cdot 9615:1:0\cdot 7050]$.

Thallous malonate, $Tl_2C_3H_2O_4$, is very soluble in water, and separates only from highly supersaturated solutions in large, transparent, monoclinic crystals $[a:b:c = 0\cdot 5707:1:1\cdot 0833$; $\beta = 81°30\frac{1}{3}']$.   E. H. R.

Hyposulphites. X. Diformaldehydesulphoxylic Acid [Hydroxymethyl Hyposulphite]. A. BINZ [with R. HUETER and E. GOLDENZWEIG] (*Ber.*, 1917, **50**, 1274—1286. Compare A., 1915, i, 801).

—Sodium formaldehydesulphoxylate (rongalite) reacts with formaldehyde and hydrochloric acid according to the equation
$$ONa\cdot S\cdot O\cdot CH_2\cdot OH + HCl + CH_2O = S(O\cdot CH_2\cdot OH)_2 + NaCl.$$
The product, *hydroxymethyl hyposulphite* ("diformaldehydesulphoxylic

acid "; "dihydroxydimethylene sulphoxylate"), can be obtained in the form of comparatively stable solutions, which may be concentrated by evaporation under reduced pressure. Sulphurous acid, on the other hand, only combines with one molecular proportion of formaldehyde, and then only when applied in the form of acid salts (for example, $NaHSO_3$), and the solutions decompose on evaporation. Directions are given for the preparation of 30% solutions from formalin or 79% solutions from methyl-alcoholic formaldehyde.

The new substance reacts with one molecular proportion of potassium hydroxide to give potassium formaldehydesulphoxylate and formaldehyde, thus:

$$S(O \cdot CH_2 \cdot OH)_2 + KOH = OH \cdot CH_2 \cdot O \cdot S \cdot OK + CH_2O + H_2O.$$
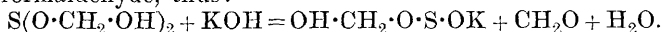
It also reacts with four atomic proportions of iodine, according to the equation $S(O \cdot CH_2 \cdot OH)_2 + 4I + 2H_2O = H_2SO_4 + 4HI + 2CH_2O.$ This disposes of the sulphone and sulphoxide formulæ, $H \cdot SO_2 \cdot H$ and $H \cdot SO \cdot OH$, for hyposulphurous acid. Bazlen has shown, however, that formaldehydesulphoxylic acid is dibasic, at any rate in its barium salt, and ascribes to the acid the formula

$$SH(OH)_2 \cdot O \cdot CH_2 \cdot OH.$$
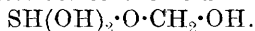
This corresponds with a hyposulphurous acid of the type $SH(OH)_3$, analogous, therefore, to $H \cdot SO \cdot OH$. In order to reconcile Bazlen's salt (A., 1905, ii, 240) with the above theories, it is assumed that the alcoholic hydrogen has acidic properties. The salt is therefore represented by $O{<}^{S---O}_{CH_2 \cdot O}{>}Ba, 2H_2O$ rather than by

$$OH \cdot CH_2 \cdot O \cdot SH{<}^{O}_{O}{>}Ba, H_2O.$$
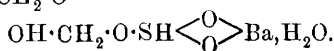
The chief difficulty connected with the formula $S(O \cdot CH_2 \cdot OH)_2$, however, is that one formaldehyde molecule is very easily eliminated, whilst the other remains until the sulphur atom is oxidised to the sexavalent condition. Perhaps it may be possible to account for this on stereochemical grounds, as in Hinsberg's theory (A., 1916, i, 725).

A solution of hydroxymethyl hydroxybenzyl hyposulphite, $OH \cdot CH_2 \cdot O \cdot S \cdot O \cdot CHPh \cdot OH$, can also be obtained, by mixing rongalite, hydrochloric acid, and benzaldehyde.

If powdered rongalite is warmed with chloromethyl methyl ether, a small yield of *hydroxymethyl methoxymethyl hyposulphite* can be obtained, as a colourless oil, thus: $OH \cdot CH_2 \cdot O \cdot S \cdot ONa + CH_2Cl \cdot OMe = OH \cdot CH_2 \cdot O \cdot S \cdot O \cdot CH_2 \cdot OMe + NaCl.$

The hydroxyl groups in the above hyposulphites can be replaced by the residues of primary amines if the esters and bases are mixed in ethereal solutions. Solid products separate as a rule. The following examples are given. Hydroxymethyl hyposulphite and ammonia give *aminomethyl hyposulphite*, $S(O \cdot CH_2 \cdot NH_2)_2$, as a sticky mass; aniline yields *anilinomethyl hyposulphite*, in white leaflets, m. p. 131° (decomp.); methyl anthranilate forms o *carbomethoxyanilinomethyl hyposulphite*,

$$S(O \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2Me)_2,$$
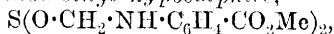
in needles, m. p. 169—171°; *p*-anisidine gives p-*methoxyanilino-methyl hyposulphite*, m. p. 105°; *o*-phenylenediamine yields o-*aminoanilinomethyl hydroxymethyl hyposulphite*,

$$OH \cdot CH_2 \cdot O \cdot S \cdot O \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot NH_2,$$
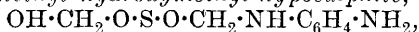
m. p. 116°. From the ethereal solution of hydroxymethyl hydroxybenzyl hyposulphite, the following compounds have been obtained: with *p*-toluidine, p-*toluidinomethyl* α-*hydroxybenzyl hyposulphite*, m. p. 125—126°; with anthranilic acid, o-*carboxyanilinomethyl* α-*hydroxybenzyl hyposulphite*, m. p. 168° (decomp.). The latter ester reacts with potassium cyanide to form o-*carboxyanilinoacetonitrile*, $CO_2H \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CN$, m. p. 181°.

J. C. W.

Two Crystallised Isomeric Lævulose Penta-acetates.

F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 280—282).—The two penta-acetates were prepared from a lævulose tetra-acetate, the α-form by means of zinc chloride and acetic anhydride, the β-form by strong sulphuric acid and acetic anhydride (A., 1915, i, 502).

α-Lævulose penta-acetate crystallises from a mixture of alcohol and chloroform in rhombic, bisphenoidal prisms [$a:b:c = 0.4946 : 1 : 0.3349$].

β-Lævulose penta-acetate, well-formed, rhombic, bisphenoidal crystals from ether [$a:b:c = 0.4941 : 1 : 0.9094$].

The two substances exhibit the same symmetry and one identical ratio. This ratio, $a:b$, is probably determined by a cyclic atomic structure common to both. The substances are not interconvertible, and this kind of morphotropic relationship must be caused by true chemical isomerism, in which a great part of the molecule is common to both modifications. E. H. R.

Attempts at the Biochemical Synthesis of Diglucosides of Multivalent Alcohols. β-Diglucoside of Glycol.

ÉM. BOURQUELOT and M. BRIDEL (*Compt. rend.*, 1917, **165**, 728—730). —It is shown that, by the action of emulsin on an aqueous solution of dextrose (2 mols.) and ethylene glycol (1 mol.), a mixture of glucosides and hexobioses is formed, but it was not possible to isolate the former in a crystalline state or to determine whether they were diglucosides. W. G.

The Synthesis of Two New Disaccharides and their Biological Behaviour.

FRITZ WREDE (*Biochem. Zeitsch.*, 1917, **83**, 96—102).—By the action of potassium sulphide or selenide on alcoholic solutions of β-acetobromodextrose, the octa-acetates of disaccharides are obtained, in which one of the oxygen atoms is replaced by sulphur or selenium.

These well-crystallised substances yield on hydrolysis by acids hydrogen sulphide or selenide and a reducing sugar. For the sulphur compound, $C_{28}H_{38}O_{18}S$, $[a]_D^{25} = -38.21°$, and for the selenium compound, $C_{28}H_{38}O_{18}Se$, $[a]_D^{15} = -51.24°$, in tetrachloro-

ethane solution. On hydrolysis with alcoholic ammonia, scission of the acetyl groups takes place, and the *disaccharides*, $C_{12}H_{22}O_{10}S$, m. p. $174°$, $[a]_D^{26} = -86\cdot74°$ (in water), and $C_{12}H_{22}O_{10}Se$, m. p. $193°$, $[a]_D^{26} = -83\cdot58°$, are obtained. The sugars yield crystalline metallic salts, such as the potassium salts, $C_{12}H_{21}O_{10}Se(or\ S)K + 2H_2O$ and $C_{12}H_{20}O_{10}Se(or\ S)K_2 + 4H_2O$. The sugars are only very slightly toxic, and pass through the body of mice for the most part unchanged. The sugars are very resistant to the actions of enzymes. They are designated, for reasons given by the author, as *thio-* and *seleno-isotrehalose*. S. B. S.

Pasteur's Principle of the Relation between Molecular and Physical Asymmetry. III. Racemic and Optically Active Complex Salts of Tervalent Rhodium. F. M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 244—262).—In continuation of previous investigations on the complex triethylenediamine salts of cobalt (A., 1915, ii, 399), corresponding salts of rhodium have now been examined crystallographically.

Sodium rhodium chloride, $\{RhCl_6\}Na_3,12H_2O$, forms blackish-red, massive, apparently octahedral crystals belonging to the monoclinic system $[a:b:c = 1\cdot2034:1:1\cdot4576\ ;\ \beta = 57°9\tfrac{1}{2}']$.

r-Triethylenediaminerhodium chloride, $[Rh(C_2H_8N_2)_3]Cl_3,3H_2O$, forms strongly refracting prisms of ditetragonal scalenohedral symmetry $[a:c = 1:0\cdot6730]$. The substance is perfectly isomorphous with the corresponding cobalti-salt, Werner's supposition that it is cubic, forming mixed crystals with sodium chloride, being erroneous.

r - Triethylenediaminechromi-chloride, $[Cr(C_2H_8N_2)_3]Cl_3,3H_2O$, forms orange, transparent, lustrous prisms, isomorphous with the previous compound $[a:c = 1:0\cdot6930]$.

l-Triethylenediaminerhodium chloro-*d*-tartrate,

$$[Rh(C_2H_8N_2)_3]Cl(C_4H_4O_6),4H_2O,$$
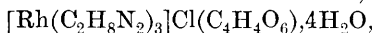
colourless, monoclinic plates or prisms $[a:b:c = 0\cdot9158:1:0\cdot6965\ ;\ \beta = 72°35\tfrac{2}{3}']$.

l-Triethylenediaminerhodium bromide, $[Rh(C_2H_8N_2)_3]Br_3,2H_2O$, colourless ditetragonal, apparently bipyramidal, prisms, isomorphous with the corresponding cobalti-salt $[a:c = 1:0\cdot8330]$. No indication of hemihedrism was observed.

r - Triethylenediaminerhodium iodide, $[Rh(C_2H_8N_2)_3]I_3,H_2O$, small, colourless, rhombic bipyramidal crystals, isomorphous with the corresponding cobalti-salt $[a:b:c = 0\cdot8541:1:0\cdot8632]$.

l-Triethylenediaminerhodium iodide, $[Rh(C_2H_8N_2)_3]I_3,\tfrac{1}{2}H_2O$ (?), is undoubtedly isomorphous with the corresponding cobalti-salt, although this contains one molecule of water of crystallisation. The small, well-developed crystals are rhombic $[a:b:c = 0\cdot8064:1:0\cdot7380]$, but the expected bisphenoidal character is not exhibited in any distinct way, any more than in the case of the optically active cobalti-salt.

r-Triethylenediaminerhodium nitrate, $[Rh(C_2H_8N_2)_3](NO_3)_3$, is

isomorphous with the cobalti-salt, rhombic pyramidal $[a:b:c = 0\cdot7874:1:0\cdot5606]$. The crystals are always distinctly hemimorphic, a being the polar axis.

l-Triethylenediaminerhodium nitrate, also isomorphous with the cobalti-salt, forms rhombic crystals, variously distorted and distinctly bisphenoidal in character $[a:b:c=0\cdot8642:1:0\cdot6049]$.

Tables and curves showing the optical rotations and dispersions of solutions of the optically active salts are given. The dispersion curves for the rhodium salts are very different in shape from those of the cobalti-salts, whilst the absolute rotation values are much greater for the latter.

The optically active salts do not in general exhibit the hemihedral characters which would be anticipated from a rigid application of Pasteur's principle. It is concluded that chemical identity of the asymmetrically arranged substituents around the central atom is unfavourable for the development of enantiomorphism in the crystals. The asymmetry as such chiefly determines the size of the optical rotation, whilst chemical contrast between the different substituents determines the manifestation of crystal enantiomorphism.

A great deal of evidence is advanced that, contrary to Werner's view, the same configuration must be attributed to corresponding optically active complex salts of cobalt and rhodium when these exhibit a rotation in the same direction.   E. H. R.

Some Isomeric Complex *cis-* **and** *trans-***Diethylenediamine Salts of Cobalt, and Triethylenediamine Zinc Chloride.** F. M. JAEGER and JUL. KAHN (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 292—303).—According to Werner's theory, compounds containing complex ions of the type $(MeX_4'Y_2')$ must exist in two isomeric forms, of which the *cis*-form alone is resolvable into optical antipodes. Several *cis-* and *trans*-isomerides are here described crystallographically.

r-*cis*-Diamminodiethylenediaminecobaltichloride,

$$[Co(NH_3)_2(C_2H_8N_2)_2]Cl_3,H_2O,$$
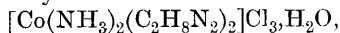
reddish-brown, lustrous plates, isomorphous with the corresponding bromide and iodide. Monoclinic prismatic $[a:b:c=1\cdot1172:1:0\cdot8325;\ \beta=87°56\frac{1}{3}']$. The bromide has $[a:b:c=1\cdot1177:1:0\cdot8322;\ \beta=88°5']$, and the iodide $[a:b:c=1\cdot0975:1:0\cdot8178;\ \beta=87°28\frac{2}{3}']$. The crystals of all three salts are weakly dichroic.

trans-Diamminodiethylenediaminecobalti-iodide, small, ill-developed, hexagonal-shaped plates, rhombic bipyramidal $[a:b:c=1\cdot2449:1:1\cdot2842]$.

r-*cis*-Diamminodiethylenediaminecobaltinitrate,

$$[Co(NH_3)_2(C_2H_8N_2)_2](NO_3)_3,$$
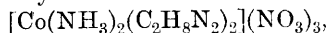
well-formed, reddish-brown pyramids, rhombic bipyramidal $[a:b:c=0\cdot9473:1:0\cdot6758]$.

r-*cis*-Dinitrodiethylenediaminecobaltinitrate,

$$[Co(NO_2)_2(C_2H_8N_2)_2](NO_3),$$
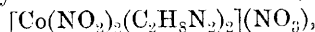
small, yellowish-red prisms, monoclinic prismatic $[a:b:c=1\cdot5589:$ $1:0\cdot4073\,;\ \beta=68°30\frac{3}{4}']$.

trans-Dinitrodiethylenediaminecobaltinitrate, from the mother liquor of the *cis*-isomeride, forms well-developed, lustrous, reddish-brown crystals, monoclinic prismatic $[a:b:c=1\cdot3040:1:1\cdot0085\,;$ $\beta=73°31\frac{1}{4}']$.

r-*cis*-Dinitrodiethylenediaminecobaltinitrite,

$$[Co(NO_2)_2(C_2H_8N_2)_2](NO_2),$$
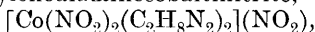
well-developed, dark crystals, monoclinic prismatic $[a:b:c=0\cdot7382:$ $1:0\cdot9094\,;\ \ \beta=82°57']$. The corresponding *trans*-isomeride contains $2H_2O$, and forms large, well-developed prisms, which quickly effloresce. It is monoclinic prismatic $[a:b:c=1\cdot0458:1:1\cdot7995\,;$ $\beta=68°33\frac{2}{3}']$. From a solution containing both *cis*- and *trans*-isomerides, crystals are obtained intermediate between those of the two pure individuals $[a:b:c=1\cdot0169:1:0\cdot9030\,;\ \beta=66°16']$. The ratio $a:b$ is similar to that of the *trans*-, whilst $b:c$ resembles that of the *cis*-isomeride. It is not clear whether a double compound or a mixed crystal is formed.

r-Triethylenediaminezinc chloride, $[Zn(C_2H_8N_2)_3]Cl_2,2H_2O$, forms lustrous, transparent crystals, monoclinic prismatic $[a:b:c=$ $0\cdot9238:1:0\cdot6299\,;\ \ \beta=86°33']$. Attempts to resolve the racemic compounds are being made. E. H. R.

The Catalytic Reduction of ω-Nitrostyrenes. ADOLF SONN and ALBERT SCHELLENBERG (*Ber.*, 1917, **50**, 1513—1525).—On reduction in alcoholic suspension with a molecular proportion of hydrogen in the presence of platinum-black, ω-nitrostyrene is converted into a mixture of isomeric, probably stereoisomeric, compounds of the composition $C_{16}H_{16}O_4N_2$; the less soluble product is *αδ-dinitro-βγ-diphenylbutane*, $NO_2\cdot CH_2\cdot CHPh\cdot CHPh\cdot CH_2\cdot NO_2$, hexagonal prisms, m. p. 238° (decomp.) [*sodium* derivative, $C_{16}H_{14}O_4N_2Na_2$; *tetrabromo*-derivative, $C_{16}H_{12}O_4N_2Br_4$, colourless prisms, m. p. 219° (decomp.); *bisphenylhydrazone*, of the corresponding butanedione, $C_2H_2Ph_2[C(NO_2)\!:\!N\cdot NHPh]_2$, orange-red prisms, m. p. 213—214° (decomp.), obtained by the action of benzenediazonium acetate on the solution of the nitro-compound in methyl alcohol containing sodium methoxide], the constitution of which is confirmed by oxidation of the sodium derivative with potassium permanganate to β-*s*-diphenylsuccinic acid. The accompanying *isomeride*, pearly scales, m. p. 190° (decomp.), is obtained in small quantity, but its stereoisomeric nature is assumed by analogy with the results with the corresponding reduction products of ω-nitro-3:4-methylenedioxystyrene; the two dinitrodiphenylbutanes are distinguished by the prefixes α- and β-. If the ω-nitrostyrene is reduced similarly, but in acetic acid instead of alcohol, the chemical change is more vigorous and proceeds somewhat differently, only the α-modification of the dinitrodiphenylbutane being obtained, together with phenyl-acetaldoxime and an amorphous mixture of substances.

ω-Nitro-3:4-methylenedioxystyrene, when reduced in alcoholic

suspension by hydrogen and platinum-black yields the α- and β-modifications of $\alpha\delta$-*dinitro-$\beta\gamma$-bis*[-3 : 4-*methylenedioxyphenyl*]-*butane*, $NO_2 \cdot CH_2 \cdot CH(C_6H_3 \cdot O_2 \cdot CH_2) \cdot CH(C_6H_3 \cdot O_2 \cdot CH_2) \cdot CH_2 \cdot NO_2$; the α-form crystallised in prisms, m. p. 249° (decomp.) (*disodium* derivative, $C_{18}H_{14}O_8N_2Na_2$; *tetrabromo*-derivative, $C_{18}H_{12}O_8N_2Br_4$, needles, m. p. 201° (decomp.); *bisphenylhydrazone* of the corresponding butanedione,

$$CH_2 \cdot O_2 \cdot C_6H_3 \cdot CH \cdot C(NO_2) \cdot N \cdot NHPh$$
$$CH_2 \cdot O_2 \cdot C_6H_3 \cdot CH \cdot C(NO_2) \cdot N \cdot NHPh'$$
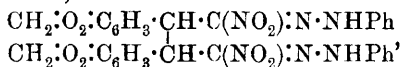
leaflets, m. p. 209° with decomp., obtained by the action of benzene-diazonium acetate on the disodium compound). The disodium derivative in aqueous solution was oxidisable by potassium permanganate, with formation of s-*di*(-3 : 4-*methylenedioxyphenyl*)-*succinic* *acid*, $CH_2 \cdot O_2 \cdot C_6H_3 \cdot CH(CO_2H) \cdot CH(CO_2H) \cdot C_6H_3 \cdot O_2 \cdot CH_2$, colourless prisms, m. p. 259° (decomp.), of which the *tin, lead, mercury, bismuth*, and *silver* salts were prepared by precipitation. The β-*stereoisomeride*, $C_{18}H_{16}O_8N_2$, pale yellow rhombic tablets, m. p. 173° (decomp.), like the α-compound, forms a *tetrabromo*-derivative, $C_{18}H_{12}O_8N_2Br_4$, pale yellow tablets or prisms, and a *disodium* derivative, $C_{18}H_{14}O_8N_2Na_2$, which reacts with benzenediazonium acetate, yielding a *bisphenylhydrazone*, $C_{30}H_{24}O_8N_6$, needles, m. p. 186°.

Reduction of ω-nitro-3 : 4-methylenedioxystyrene in alcohol by hydrogen and colloidal palladium also gives the α- and β-modifications of dinitrodi(methylenedioxyphenyl)butane, whilst reduction in acetic acid with hydrogen and platinum yields the α-stereoisomeride, together with homopiperonaldioxime and resinous products.   D. F. T.

Derivatives of *n*-Butylaniline. JOSEPH REILLY and WILFRID JOHN HICKINBOTTOM (T., 1917, **111**, 1026—1034).—*n*-Butylaniline has been obtained by heating together aniline and *n*-butyl chloride, and converted by well-known methods into the following series of compounds: *A*, phenyl-*n*-butylnitrosoamine, phenyl-*n*-butylhydrazine, and diphenyldi-*n*-butyltetrazone, $C_6H_5 \cdot N(C_4H_9) \cdot NO \longrightarrow$ $C_6H_5 \cdot N(C_4H_9) \cdot NH_2 \longrightarrow C_4H_9 \cdot NPh \cdot N \cdot N \cdot NPh \cdot C_4H_9$; *B*, *p*-nitroso-*n*-butylaniline, *p*-phenylene-*n*-butyldiamine, and *p*-nitrosophenyl-*n*-butylnitrosoamine, $NH_2 \cdot C_6H_4 \cdot NH \cdot C_4H_9 \longleftarrow NO \cdot C_6H_4 \cdot NH \cdot C_4H_9$ $\longrightarrow NO \cdot C_6H_4 \cdot N(C_4H_9) \cdot NO$.

For experimental details, see original.   J. C. W.

Bromides of Schiff's Bases. HARTWIG FRANZEN, HENRYK WEGRZYN, and MEER KRITSCHEWSKY (*J. pr. Chem.*, 1917, [ii], **95**, 374—391. Compare A., 1914, i, 162; 1915, i, 230; 1917, i, 644). —In earlier papers, it has been shown that the dibromides of Schiff's bases suffer rearrangement into benzylidene-*p*-bromoanilines when boiled with alcohol or treated with pyridine. Frequently, it was found that the original dibromides contained an excess of halogen, and consequently gave mixed products on rearrangement. The bromination of benzylideneaniline and benzylidene-*p*-toluidine

has therefore been investigated more closely. These Schiff's bases have been dissolved in various media, the solutions cooled by ice, and bromine slowly added in the pure or diluted state, equimolecular quantities being employed. The precipitates have then been collected and analysed.

With ether and carbon disulphide alone is it possible to obtain pure products, and with these, dibromides and tribromides are formed. The dibromides can only have the formula

CHPhBr·NRBr,
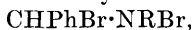
but the constitution of the tribromides remains in doubt. The extra bromine atom is not attached to one of the nuclei, neither has it replaced hydrogen in the –CHPh– grouping. It appears to be attached to nitrogen, as in the perhaloids of tertiary amines.

Ethereal Solution.—Benzylideneaniline gives with undiluted bromine the bright yellow *tribromide*, $C_{13}H_{11}NBr_3$, m. p. 156—157° (decomp.), and some of the lemon-yellow dibromide, m. p. 203—207°, which separates from the first filtrate. If the bromine is diluted with carbon disulphide, the dibromide only is precipitated. Benzylidene-*p*-toluidine gives a deep yellow *tribromide*, $C_{14}H_{13}NBr_3$, golden-yellow leaflets, m. p. 168—172°, under both conditions.

Carbon Disulphide Solution.—Benzylideneaniline yields the pure dibromide, and benzylidene-*p*-toluidine the pure tribromide.

Benzene Solution.—Benzylideneaniline forms a brick-red dibromide, containing bromine in excess of the theoretical amount; benzylidene-*p*-toluidine gives the tribromide.

Chloroform Solution.—Benzylideneaniline gives a mixture of di- and tri-bromide; benzylidene-*p*-toluidine forms in dilute solutions a yellow powder, containing more bromine than a tetrabromide, and in more concentrated solutions a mixture of di- and tri-bromide.

Light Petroleum Solution.—Benzylideneaniline deposits a bright brick-red powder, containing somewhat less bromine than the dibromide; benzylidene-*p*-toluidine gives a similar reddish-yellow powder.

Glacial Acetic Acid Solution.—Benzylideneaniline forms a mixture of mono- and di-bromides.

Benzylidenebenzylamine, in chloroform solution, also yields a brick-red *tribromide*, m. p. 149°. This reacts with aqueous ammonia according to the scheme: $C_{14}H_{13}NBr_3 \longrightarrow C_6H_5\cdot CN + NH_2\cdot CH_2Ph + NH_4Br$. The absence of brominated benzene derivatives among the products is evidence that the third bromine atom in these tribromides is not attached to a benzene nucleus. The compound liberates one atomic proportion of iodine from acidified potassium iodide. J. C. W.

The Reciprocal Exchange of Aromatically Combined Hydroxyl and Halogen. W. Borsche [with Hugo Löwenstein and Rudolf Quast] (*Ber.*, 1917, **50**, 1339—1355).—In a recent

paper (A., 1917, i, 15), it was shown that the *p*-nitro group in halogeno-2:4-dinitrobenzene can be substituted by the cyano, acetyl, or benzoyl group without seriously lessening the reactivity of the halogen atom. It has now been tested whether these groups can replace one of the nitro-groups in dinitrophenols without hindering the exchange of the hydroxyl group by chlorine in Ullmann's reaction (A., 1908, i, 524). Even in the least unfavourable case, namely, when a cyano-group is in the para-position of an *o*-nitrophenol, the replaceability of the hydroxyl group is considerably lessened.

When 3-nitro-4-hydroxybenzonitrile is heated with *p*-toluenesulphonyl chloride and diethylaniline, a considerable quantity of the p-*toluenesulphonate*, $NO_2 \cdot C_6H_3(CN) \cdot O \cdot SO_2 \cdot C_6H_4Me$, is obtained, in pale yellow leaflets, m. p. 139—141°, but about 5% of 4-chloro-3-nitrobenzonitrile is formed. This is identified by conversion into 2-nitro-4-cyanodiphenylamine.

5-*Nitro*-**4**-*hydroxytoluonitrile*, pale yellow needles, m. p. 132—133°, gives only the p-*toluenesulphonate*, sparkling crystals, m. p. 137—138°. This new substituted cresol is obtained as follows: *p*-homosalicylaldehyde is nitrated in cold, glacial acetic acid, the nitro-aldehyde is converted into the oxime, m. p. 214—216°, and this is boiled with acetic anhydride. The 3-*nitro-5-cyano*-p-*tolyl acetate*, m. p. 136°, so formed is hydrolysed by contact with 2% potassium hydroxide.

3-*Nitro*-4-*hydroxy*-5-*methoxybenzonitrile*, white needles, m. p. 140°, also only yields the p-*toluenesulphonate*, m. p. 104°. The new substituted guaiacol is prepared as follows: acetylvanillonitrile is slowly added to well-cooled, fuming nitric acid, and the product, 2-*nitro*-4-*cyano*-6-*methoxyphenyl acetate*, slender, pale yellow needles, m. p. 102°, is hydrolysed.

Comparing 3-nitro-4-hydroxybenzonitrile with 3-nitro-4-hydroxy-5-methoxybenzonitrile, it appears, therefore, that the mobility of the hydroxyl group, which is already much less than it is in the case of 2:4-dinitrophenol, is completely suppressed by the proximity of the methoxy-group. In the case of dinitroguaiacol, however, the methoxy-group does not exert such an influence. When this compound (4:6-dinitro-2-methoxyphenol) is treated with *p*-toluenesulphonyl chloride and sodium carbonate, it yields the p-*toluenesulphonate*, prisms, m. p. 137—138°, but it reacts with the chloride in the presence of diethylaniline to give, in addition to a small amount of this ester, 2-*chloro*-3:5-*dinitroanisole*,

$$OMe \cdot C_6H_2Cl(NO_2)_2,$$
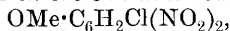
which crystallises in greenish-yellow leaflets, m. p. 93—94°. This chloride has been converted by the usual methods into the following compounds: (*A*) 4:6-*dinitro*-2-*methoxydiphenylamine*, golden-yellow needles, m. p. 156°; (*B*) 3:5-*dinitro*-o-*anisidine*, orange-coloured needles, m. p. 176°, which may be reduced by ammonium sulphide to 5-*nitro*-2-*methoxy*-o-*phenylenediamine*, dark red needles, m. p. 131—132°, and then condensed with benzil to form 7-*nitro*-

5-methoxy-2 : 3-*diphenylquinoxaline* (annexed formula), in yellow needles, m. p. 207—208°; (*C*) 6-*nitro*-4-*methoxy*-2-*phenyl*-ψ-*aziminobenzene*,

OMe

NO₂

-N:CPh
-N:CPh

$$NO_2 \cdot C_6H_2(OMe) < {}^{N}_{N} > NPh,$$
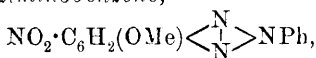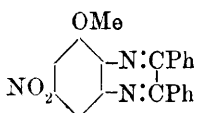
sulphur-yellow, felted needles, m. p. 191°; (*D*) *ethyl* 4 : 6 - *dinitro* - 2 - *methoxyphenylmalonate*, stout, yellow crystals, m. p. 68—69°, which may be hydrolysed by dilute sulphuric acid to 4 : 6-*dinitro*-2-*methoxyphenylacetic acid*, pale brown needles, m. p. 174—175° (evolution of carbon dioxide), *methyl* ester, m. p. 68—69°.

The usual methods for the replacement of halogen by hydroxyl in halogenonitrobenzenes leave much to be desired. Alkali hydroxides are out of the question when cyano, acetyl, carboxylic ester, or similar groups are present, and metallic acetates react so sluggishly. Heating with anhydrous sodium acetate and acetamide at 170—200°, however, often gives excellent results, and several applications of this method are now described.

1-Chloro-2 : 4-dinitrobenzene is unattacked by water at 200°, or by crystallised sodium acetate in an open vessel at 210°. When heated with 25% sodium acetate solution in a sealed tube at 200°, it is soon completely converted into 2 : 4-dinitrophenol. It only reacts with silver acetate, also in the presence of water, at 200°, giving the phenol and a small quantity of a substance, m. p. 216° (decomp.), which is most probably 2 : 4 : 2′ : 4′-tetranitrodiphenyl ether.

1-Chloro-2 : 6-dinitrobenzene gives an almost quantitative yield of 2 : 6-dinitrophenol when heated with anhydrous sodium acetate and acetamide at 170°, and 3-chloro-4 : 6-dinitrotoluene gives 4 : 6-dinitro-*m*-cresol, mixed with considerable quantities of amorphous products, due to reactions between the adjacent nitro and methyl groups.

1 : 3-Dichloro-4 : 6-dinitrobenzene reacts with 25% sodium acetate solution at 190—195°, or with the acetamide mixture at 160°, to give 3-*chloro*-4 : 6-*dinitrophenol*, in flat, yellow needles, m. p. 92°. At higher temperatures, complete decomposition sets in, and no dinitroresorcinol can be isolated from the product.

5-Chloro-2 : 4-dinitroanisole, from 1 : 3-dichloro-4 : 6-dinitrobenzene and sodium methoxide solution, reacts with the acetamide mixture to form 4 : 6-dinitro-3-methoxyphenol.

3-Chloro-4 : 6-dinitrodiphenyl ether, from 1 : 3-dichloro-4 : 6-dinitrobenzene and potassium phenoxide, reacts with aniline to form 4 : 6-*dinitro*-3-*phenoxydiphenylamine*, elongated, orange-red rhombs, m. p. 151·5°, and with the above mixture to give 4 : 6-*dinitro*-3-*phenoxyphenol*, flat, brownish-yellow needles, m. p 117—118°.

1 : 3-Dichloro-4 : 6-dinitrobenzene reacts with alcoholic dimethylamine solution to give a mixture of 4 : 6-*dinitrotetramethyl*-m-*phenylenediamine* and 3-chloro-4 : 6-dinitrodimethylaniline, which are very difficult to separate. Only the latter reacts with the

acetamide mixture, however, and the product is easily separated by ammonia solution into the diamine, yellow needles, m. p. 191°, and 4 : 6-*dinitro-3-hydroxydimethylaniline*, dark yellow needles, m. p. 152°. [Lippmann and Fleissner's compound, m. p. 195°, is really 2 : 4-*dinitro-3-hydroxydimethylaniline* (A., 1885, 1212)]. Pure 3-*chloro*-4 : 6-*dinitrodimethylaniline*, long, yellow needles, m. p. 129°, is prepared by heating the dichlorodinitrobenzene with an alcoholic solution of dimethylamine and glacial acetic acid.

5-Chloro-2 : 4-dinitrophenyl-1′-piperidine (A., 1914, i, 30) yields 4 : 6-*dinitro-3-hydroxyphenyl*-1′-*piperidine*, $C_5H_{10}N \cdot C_6H_2(NO_2)_2 \cdot OH$, in stout, orange-red crystals, m. p. 100—101°.

3-Chloro-4 : 6-dintrodiphenylamine gives 4 : 6-*dinitro-3-hydroxy-diphenylamine*, in bundles of long, dark yellow needles, m. p. 139°; 4-bromo-3-nitrobenzonitrile also readily yields 3-nitro-4-hydroxy-benzonitrile; 4-bromo-3-nitroacetophenone reacts less readily, but gives 3-*nitro*-4-*hydroxyacetophenone*, slender needles, m. p. 130°; 4-bromo-3-nitrobenzophenone changes smoothly into 3-*nitro*-4-*hydroxybenzophenone*, which crystallises in yellowish-brown rhombs, m. p. 120—121°.

In the above reactions, the acetamide merely plays the part of a most suitable solvent with high b. p., and a source of water for the hydrolysis of the acetates obtained by the interaction of the sodium acetate and the halogen compounds. Its behaviour as a hydrolytic agent is exemplified further by the facts that 2 : 4-dinitrophenyl acetate is converted into 2 : 4-dinitrophenol, and 2 : 4-dinitroacetanilide into 2 : 4-dinitroaniline, by heating with acetamide at 200°.   J. C. W.

β-Methylated Cinnamic Acids. S. LINDENBAUM (*Ber.*, 1917, **50**, 1270—1274).—The author has had occasion to prepare β-methylcinnamic acids in recent years, and had used the identical method which Stoermer, Grimm, and Laage described recently (A., 1917, i, 647). An acetophenone is mixed with ethyl bromo-acetate and zinc in benzene, whereby an ethyl β-hydroxy-β-aryl-butyrate, $OH \cdot CMeAr \cdot CH_2 \cdot CO_2Et$, is formed. In many cases, this loses water on distillation, but a preliminary boiling with phosphoryl chloride in benzene ensures this. In the cases of aceto-phenone itself, and *o*-methoxyacetophenone, the primary hydr-acrylates can be isolated in a pure state, but substituents in the para-position (for example, methyl, and especially methoxyl) lower the stability of these esters.

Four examples of the reaction are described, but the products were described by Stoermer and earlier workers.   J. C. W.

Steric Hindrance. S. REICH [and (MME.) R. SALZMANN and D. KAWA] (*Bull. Soc. chim.*, 1917, [iv], **21**, 217—225).—The reactivity of the three di-ortho-substituted aldehydes, 2 : 6-dinitrobenz-aldehyde, 2 : 6-dichlorobenzaldehyde, and 2 : 4 : 6-trimethylbenz-aldehyde, increases as the weight of the substituent group increases. With 2 : 6-dichlorobenzaldehyde, an intermediate product, 2 : 6-*di*-

chlorobenzylidene diacetate, needles, m. p. 85°, can be isolated, which by the further action of sodium acetate and acetic anhydride at 180° yields 2 : 6-*dichlorocinnamic acid*, slender needles, m. p. 184°, from which by the action of bromine in acetic acid, *αβ-dibromo-β-2 : 6-dichlorophenylpropionic acid*,

$$C_6H_3Cl_2 \cdot CHBr \cdot CHBr \cdot CO_2H,$$
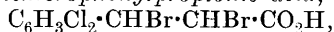
m. p. 184°, is obtained. This acid yields, with alcoholic potassium hydroxide, 2 : 6-*dichlorophenylpropiolic acid*, $C_6H_3Cl_2 \cdot C\dot{:}C \cdot CO_2H$, m. p. 167—168°, and 2 : 6-*dichlorophenylacetylene*, $C_6H_3Cl_2 \cdot C\dot{:}CH$, m. p. 100°. These on bromination give respectively *αβ-dibromo-2 : 6-dichlorophenylacrylic acid*, m. p. 171—172°, and *αβ-dibromo-2 : 6-dichlorophenylstyrene*, m. p. 70—71°.

The ease of esterification of benzoic acid is decreased one hundred and sixty-three times by the introduction of two chlorine atoms into the ortho-positions, whilst the reactivity of ethyl benzoate towards magnesium phenyl bromide is only diminished fourteen times by a similar introduction of chlorine atoms. On the other hand, 2 : 6-dichlorobenzaldehyde easily reacts with Grignard's reagent, giving 2 : 6-*dichlorodiphenylcarbinol*,

$$C_6H_3Cl_2 \cdot CHPh \cdot OH,$$

m. p. 57°, giving an *acetate*, m. p. 105°.

The two di-ortho-substituted anilines, 2 : 4 : 6-trinitro- and 2 : 4 : 6-tribromo-aniline, do not condense with benzaldehyde (compare Hantzsch, A., 1891, 68), but 2 : 6-dinitro- an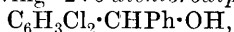d 2 : 6-dichlorobenzaldehyde both condense readily with aniline. 2 : 6-*Dichlorobenzylideneaniline* crystallises in pale yellow needles, m. p. 64—65°.

2 : 6-Dichlorobenzaldehyde gives an o-*nitrophenylhydrazone*, red needles, m. p. 154°, a p-*bromophenylhydrazone*, brown needles, m. p. 142°, and an *oxime*, colourless needles, m. p. 146—147°. The last compound, when boiled with acetic anhydride for five minutes, gives 2 : 6-*dichlorobenzonitrile*, m. p. 143° [the compound, m. p. 49°, described by Claus and Stavenhagen (compare A., 1892, 1206) under this name is not this nitrile], which is only very slightly hydrolysed by heating for three hours with 60% sulphuric acid at 150°. With hydrogen peroxide in alkaline solution, it yields 2 : 6-*dichlorobenzamide*, m. p. 202°. Schultz (compare this Journal, 1872, 1005) describes such a compound, m. p. 166°, but the dichlorobenzoic acid with which he started did not possess the properties now ascribed to 2 : 6-dichlorobenzoic acid. W. G.

Nitration of Benzoylformic [Phenylglyoxylic] Acid. S. REICH and P. MOREL (*Bull. Soc. chim.*, 1917, [iv], **21**, 225—226). —When phenylglyoxylic acid is slowly added to nitric acid (D 1·5) at −10°, the sole product is *m*-nitrophenylglyoxylic acid. W. G.

Keto–Enol Isomerism. III. The Isomeric Formyl phenylacetic Esters. W. DIECKMANN (*Ber.*, 1917, **50**, 1375—1386. Compare A., 1916, i, 820, 822; and Wislicenus, A., 1917, i, 268). —Recent researches have revealed the fact that ethyl formyl-phenylacetate exists in the pure state only as a liquid enol, "*a*,"

and a solid enol, "γ," m. p. 110°, and that the methyl ester like-
wise exists only as an "α"-enol, m. p. 40—41°, and a "γ"-enol,
m. p. 105° (in Jena glass capillaries; in soft glass, the m. p. may
be as low as 70°, and a trace of sodium acetate will depress it to
about 40°). Wislicenus suggested that these pairs of enols may
be *cis-trans*-isomerides, although the γ-enols do not give the ferric
chloride reaction or form a sparingly soluble copper salt. This
objection is met by reference to dimethyldihydroresorcinol, which
is certainly enolic, but does not give the ferric chloride reaction.
There are steric hindrances in each case against the formation of
"conjugated enol salts." The sodium salt of the α-enol is stable
in the dry state, but changes into the isomeride in aqueous solu-
tion. If the aqueous solution is quickly acidified, the γ-form is
obtained, but if acid is slowly added, the alkali salt still present
catalyses the transformation of the γ-form into the α-modification.

The equilibria existing between the enols and the aldo-forms,
which have not been isolated as yet, have been studied by Meyer's
method. Distilled ethyl α-formylphenylacetate, or the liquid
obtained by heating the γ-ester at 110°, is about 91% enol; the
solid γ-ester is pure enol. Crystalline methyl α-formylphenyl-
acetate is 97·4% enol, and, after melting, remains molten at the
ordinary temperature, with 87% enol; the crystalline γ-ester is
pure enol. After heating at 110° for three hours, the α-ethyl
ester drops to 78—81% enol, but reaches the above equilibrium
when kept.

The crystalline ethyl ester is present in 1% solutions in pure
formic acid, acetic acid, benzene, and hexane to the extent of 77·8,
88·6, and 97% respectively in the enolic form. In methyl alcohol,
however, the esters appear to exist only to the extent of about 8%
as enols, and in ethyl alcohol only 22%, but this is due to the
formation of additive compounds with the solvents (compare
Wislicenus). The speed of the reaction with alcohols can be
ascertained by the titration method. It is about seven times as
great for the γ-esters as for the α-esters, and about 1·7 times as
great for methyl alcohol as for ethyl alcohol; it is greatly
accelerated, in the same degree, by hydrogen chloride, which has
no pronounced effect on the transformation of one enol into the
other. Alkaline agents and pyridine also catalyse the reaction
with alcohol in proportion to their "alkalinity," but they soon
bring the speed of the reaction to the same level for both α- and
γ-esters. Accordingly, alkaline agents expedite the transformation
of γ- into α-forms, most probably through the aldo-modifications.

Ethyl formylphenylacetate (α or γ) does not give a colour with
concentrated sulphuric acid and thiophen-benzene until it has
been exposed to the air, when it gives the red to deep blue colour
characteristic of phenylglyoxylic acid. Auto-oxidation does,
indeed, take place according to the equation $OH \cdot CH\!:\!CPh \cdot CO_2R + O_2 = C_6H_5 \cdot CO \cdot CO_2R + H \cdot CO_2H$, and the presence of the phenyl-
glyoxylate in the product may be fully established (hydrazone; free
acid and its *silver* salt, hydrazone and anil). Oxidation to phenyl-

glyoxylic acid is also immediately brought about by alkaline permanganate (compare Michael, A., 1912, i, 861).

The esters are decomposed by boiling with 90% acetic acid into the alcohol, carbon dioxide, and phenylacetaldehyde, which may be identified as the semicarbazone.   J. C. W.

Semicarbazones of α-Ketonic Acids. α-Iodocinnamic Acids; αα-Di-iodo- and Dibromo-phenylbutyric Acids; α-Iodo- and α-Bromo-phenylcrotonic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1917, [iv], **21**, 246—258).—The first part of the paper is a more detailed account of work already published (compare A., 1916, i, 817; 1917, i, 26, 647). *α-Iodo-γ-hydroxy-βγ-diphenylcrotonic acid*, HO·CHPh·CPh:CI·CO₂H, m. p. 190°, is obtained by the action of iodine on an alkaline solution of the semicarbazone of α-keto-βγ-diphenylbutyrolactone, there being no intermediate formation of a di-iodo-acid and only the one α-iodo-acid. This acid when reduced with zinc and acetic acid gives a mixture of *γ-hydroxy-βγ-diphenylcrotonic acid*, m. p. 161°, and diphenylcrotonolactone, m. p. 151°. *α-Bromo-γ-hydroxy-βγ-diphenylcrotonic acid*, m. p. 192°, is similarly prepared using an alkaline solution of sodium hypobromite.

By the hydrolysis of αα-dibromophenylbutyramide and of αα-dibromophenylpropionamide with hydrochloric acid, the author has obtained respectively αα-dibromophenylbutyric acid and α-bromocinnamic acid.   W. G.

The Phenylsuccinic Acid Series. V. Interconversion of the Esters of r- and *meso*-Diphenylsuccinic Acids. HENRY WREN and CHARLES JAMES STILL (T., 1917, **111**, 1019—1025. Compare A., 1917, i, 456).—The interconvertibility of r- and *meso*-diphenylsuccinic acids has been known for some years. It is now shown, at the instance of the methyl and ethyl compounds, that the esters readily undergo mutual transformation. Interconversion may be effected by hydrolysis with an insufficiency of alcoholic potassium hydroxide solution or by the action of a solution of the corresponding sodium alkyloxide in the requisite alcohol, or, in some instances, by the action of a suspension of sodium alkyloxide in dry ether.

meso-Diphenylsuccinic acid is slowly converted into the r-acid by prolonged treatment with an excess of boiling aqueous alcoholic potassium hydroxide solution, but the reverse change could not be shown to occur.   H. W.

Action of Organo-magnesium Compounds on Apiolealdehyde. Preparation of Apiolealdehyde. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1917, **50**, 1335—1339).—Some years ago, the authors found that asarylaldehyde reacts with organo-magnesium compounds to give, not the usual carbinols, but their ethers (A., 1906, i, 424). The closely related apiolealdehyde yields both classes of derivatives, according to the conditions of the reaction.

Apiolealdehyde (4 : 5-dimethoxy-2 : 3-methylenedioxybenzaldehyde)

is best prepared by oxidising *iso*apiole with ethyl nitrite and hydrochloric acid. Asarone is conveniently oxidised to asarylaldehyde by the same method.

For the preparation of carbinols, the Grignard reaction is carried out at a low temperature, and the magnesium compound is decomposed by just sufficient dilute acid. The ethers are formed when the reaction proceeds in warm solvents and the metallic compound is decomposed by an excess of dilute sulphuric acid. Magnesium methyl iodide yields *α*-4 : 5-*dimethoxy*-2 : 3-*methylenedioxyphenylethyl alcohol*, m. p. 52°, and its *ether*,

$$[CH_2:O_2:C_6H(OMe)_2 \cdot CHMe]_2O,$$
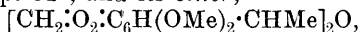
m. p. 122°; magnesium ethyl iodide gives *α*-4 : 5-*dimethoxy*-2 : 3-*methylenedioxyphenylpropyl alcohol*, m. p. 54°, and its *ether*, m. p. 112°; and *phenyl*-4 : 5-*dimethoxy*-2 : 3-*methylenedioxyphenylmethyl alcohol*, $C_9H_9O_4 \cdot CHPh \cdot OH$, has m. p. 72°.   J. C. W.

Some Derivatives of Propiophenone. K. von Auwers (*Ber.*, 1917, **50**, 1177—1182).—*α*-Bromopropiophenone has b. p. 136—137°/16 mm., D_4^{20} 1·430, n_D^{20} 1·5716, $E\Sigma_a +0·52$, $E\Sigma_D +0·55$, $E\Sigma_\beta - \Sigma_a + 37\%$, $E\Sigma_\gamma - \Sigma_a + 41\%$. In its reactions with bases and ketone reagents, this compound is usually just as much attacked at the bromine atom as at the carbonyl group, if not more so. With excess of alcoholic *p*-nitrophenylhydrazine hydrochloride, for example, it reacts on boiling to form the di-*p*-nitrophenylhydrazone of phenyl methyl diketone (below), but it behaves in a slightly abnormal way with one molecular proportion of the salt in alcohol at 40°. Under these conditions, a small quantity of *phenyl α-ethoxyethyl ketone* p-*nitrophenylhydrazone*,

$$OEt \cdot CHMe \cdot CPh:N \cdot NH \cdot C_6H_4 \cdot NO_2,$$
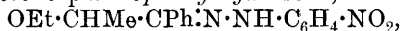
may be isolated, in pale yellow, glassy needles, m. p. 97—98°. 3-*α*-Bromopropionyl-*p*-cresol reacts more readily under these conditions, giving m-4-*hydroxytolyl α-ethoxyethyl ketone* p-*nitrophenylhydrazone*, golden-yellow, flat needles, m. p. 178—180°.

α-Acetoxypropiophenone, b. p. 143—147°/17 mm., D_4^{20} 1·112, n_D^{20} 1·5153, $E\Sigma_a +0·53$, $E\Sigma_D +0·53$, $E\Sigma_\beta - E\Sigma_a +26\%$, is readily obtained from the bromo-compound and converted into *α*-hydroxypropiophenone (phenyl *α*-hydroxyethyl ketone), $OH \cdot CHMe \cdot COPh$. This compound was obtained by Zincke and Zahn (A., 1910, i, 317) by the oxidation of methylphenylethyleneglycol, but they were more inclined to regard it as the isomeride,

$$OH \cdot CHPh \cdot COMe.$$

The identity of the two preparations is fully established by optical means. The ketone has b. p. 125—126°/14 mm., D_4^{20} 1·1065, n_D^{20} 1·5355, $E\Sigma_a +0·37$, $E\Sigma_D +0·38$, $E\Sigma_\beta - \Sigma_a +24\%$ (averages), and forms a semicarbazone, m. p. 188—189°. With *p*-nitrophenylhydrazine hydrochloride and alcohol in the cold, it forms the p-*nitrophenylhydrazone*, orange-yellow, flat, glassy needles, m. p. 179—180°, but with an excess of the reagent in hot solutions it gives the di-p-*nitrophenylhydrazone* of *phenyl methyl diketone*, a dark red, crystalline powder, m. p. 256—257°. *α*-Hydroxypropio-

phenone, or, better still, phenyl methyl diketone, reacts with o-phenylenediamine in boiling acetic acid to form 3-*phenyl*-2-*methylquinoxaline*, $C_6H_4\begin{smallmatrix}N{:}CMe\\ |\\ N{:}CPh\end{smallmatrix}$, m. p. 57—58°.   J. C. W.

The Sulphonation of Chalkones [Phenyl Styryl Ketones]. **(The Formation of Intramolecular Oxonium Salts.)** P. PFEIFFER and P. A. NEGREANU (*Ber.*, 1917, **50**, 1465—1477).—The ease with which ketones may be sulphonated by sulphuric acid is of interest as influencing the trustworthiness of the colours observed in the formation of halochromic compounds between ketones and the acid; freshly prepared solutions of the ketones in the acid yield the unaltered ketone on dilution with water, but in some cases, such as those described below, sulphonation is sufficiently rapid to become appreciable in a few hours at the ordinary temperature.

Phenyl *p*-methoxystyryl ketone at the ordinary temperature is gradually converted by sulphuric acid into *phenyl* p-*methoxystyryl ketone-sulphonic acid*, $COPh{\cdot}CH{:}CH{\cdot}C_6H_3(OMe){\cdot}SO_3H$, yellow needles, m. p. 160—162°, which become orange-red above 140° (*ammonium* salt, yellow needles with $1H_2O$, m. p. 261°). In a similar manner, anisyl *p*-methoxystyryl ketone is converted into *anisyl* p-*methoxystyryl ketone-sulphonic acid*,

$$OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_3(OMe){\cdot}SO_3H,$$
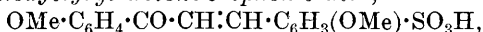
almost colourless, sometimes pale red, leaflets, m. p. indistinct near 180—181°, giving a blood-red liquid (*ammonium* salt with $2H_2O$, colourless leaflets, m. p. 279°); the constitution of this substance is demonstrated by oxidation with potassium permanganate, giving rise to a sulphoanisic acid, $OMe{\cdot}C_6H_3(SO_3H){\cdot}CO_2H{,}1\frac{1}{2}H_2O$, m. p. 236° (decomp.) (potassium salt, needles with $2H_2O$), possibly identical with the compound described by Zervas (*Annalen*, 1857, **103**, 341).

Benzylidenepaeonol reacts slowly with sulphuric acid at the ordinary temperature, giving *benzylidenepaeonolsulphonic acid*, $CHPh{:}CH{\cdot}CO{\cdot}C_6H_2(OH)(OMe){\cdot}SO_3H$, pale yellow needles with $2H_2O$, m. p. 163—164°, giving a blood-red liquid (*ammonium* salt, almost colourless needles with $2H_2O$, m. p. 256°). Phenyl anisylethyl ketone, m. p. 68° (Bargellini and Bini, A., 1911, i, 68, give 59—60°), similarly yielded *phenyl sulphoanisylethyl ketone*, $COPh{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_3(OMe){\cdot}SO_3H$, prismatic needles with $2H_2O$, m. p. 146°; *ammonium* salt, colourless needles with $1H_2O$, m. p. 245°. *Anisyl phenylethyl ketone*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4{\cdot}OMe$, prepared from anisyl styryl ketone by reduction in acetic acid with hydrogen and platinum-black, forms colourless leaflets, m. p 97° (*oxime*, colourless needles, m. p. 114°), and reacts slowly with sulphuric acid, with formation of *sulphoanisyl phenylethyl ketone*, $CH_2Ph{\cdot}CH_2{\cdot}CO{\cdot}C_6H_4(OMe){\cdot}SO_3H$, colourless needles with $5H_2O$, m. p. indefinite; *ammonium* salt, colourless needles, m. p. 270—271°. *Anisyl anisylethyl ketone*, $OMe{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}OMe$, obtained from anisyl *p*-methoxystyryl ketone in acetic acid with hydrogen and platinum-black, forms monoclinic crystals, m. p. 45°

(*oxime*, colourless needles, m. p. 119°), and with sulphuric acid at the ordinary temperature gradually forms *anisyl sulphoanisylethyl ketone*, $OMe\cdot C_6H_4\cdot CO\cdot CH_2\cdot CH_2\cdot C_6H_3(OMe)\cdot SO_3H$,   colourless needles with $3H_2O$, m. p. 149°; *ammonium* salt, colourless leaflets with $\frac{1}{2}H_2O$, m. p. 278°.

Chalkone (phenyl styryl ketone) and its methoxy-derivative, *p*-methoxyphenyl styryl ketone, resisted sulphonation by sulphuric acid at the ordinary temperature.

From a comparison of the halochromic phenomena with phenyl styryl ketone and its derivatives, the conclusion is drawn that when a sulphonic acid group is introduced in an ortho-position to a methoxyl group, the halochromic colours with sulphuric or perchloric acid revert closely to those of the methoxyl-free parent compound, so that the auxochromic effect of a methoxyl group is apparently nullified by the presence of an adjacent sulphonic acid group. This is attributed to oxonium salt formation between the two groups in question.   D. F. T.

Some Aromatic Keto-oxido-compounds. HENRIK JÖRLANDER (*Ber.*, 1917, **50**, 1457—1465. Compare A., 1917, i, 222).—The author has already applied Widman's reaction (A., 1916, i, 406, 655) to the preparation of such substances as anisoylphenylethylene oxide, and now extends it to the condensation of benzaldehyde with certain ω-halogen ketones, the general method of procedure being to add the calculated quantity of sodium ethoxide dissolved in alcohol to a cooled alcoholic mixture of the halogen ketone with a 20% excess of benzaldehyde.

ω-Dichloro-3 : 4-dimethylacetophenone and benzaldehyde gave rise to 3 : 4-*dimethylbenzoylphenylethylene oxide*,

$$\begin{matrix} O\!-\!\!-\!\!-\!\!- \\ | \quad \searrow CH\cdot CO\cdot C_6H_3Me_2, \\ CHPh \end{matrix}$$
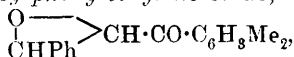
colourless prisms, m. p. 89°, which on oxidation with alkaline permanganate yielded 4-methyl*iso*phthalic acid, and on treatment with alcoholic sodium hydroxide underwent the general transformation of this class of substance with formation of o-4-*xylyl* *α-hydroxystyryl ketone*, $C_6H_3Me_2\cdot CO\cdot C(OH)\!:\!CHPh$, yellow prisms, m. p. 94—95°, which gave a deep violet-brown coloration with ferric chloride. Acetic anhydride with the addition of a little sulphuric acid converted the cyclic oxide into 3 : 4-*dimethylbenzoylphenylethylene diacetate*, $C_6H_3Me_2\cdot CO\cdot CH(OAc)\cdot CHPh\cdot OAc$, colourless prisms, m. p. 105°, which when warmed with alcoholic alkali gave benzyl o-4-xylyl ketone, $C_6H_3Me_2\cdot CO\cdot CH_2Ph$, probably produced from the free glycol by successive dehydration and intramolecular rearrangement.

ω-Chloro-2 : 4-dimethylacetophenone in the usual reaction yielded 2 : 4-*dimethylbenzoylphenylethylene oxide*, colourless leaflets, m. p. 61°, which was converted by alcoholic sodium hydroxide into m-4-*xylyl* *α-hydroxystyryl ketone*, a yellow oil, and by acetic anhydride and a little sulphuric acid into 2 : 4-*dimethylbenzoylphenylethylene diacetate*, colourless prisms, m. p. 135—136°; the

former product with o-phenylenediamine yielded 2-*benzyl*-3(2′:4′-*xylyl*)-*quinoxaline*, $C_{23}H_{20}N_2$, colourless leaflets, m. p. 126°.

Chloroacetylmesitylene, probably on account of the ortho-methyl groups, did not follow the usual course of reaction with benzaldehyde, a molecule of water undergoing elimination instead of hydrogen chloride, the product being *mesityl/yl* α-*chlorostyryl ketone*, $C_6H_2Me_3 \cdot CO \cdot CCl \colon CHPh$, colourless prisms, m. p. 86°.

p-*Phenylbenzoylphenylethylene oxide*, $\overset{O}{\underset{CHPh}{\bigg>}}CH \cdot CO \cdot C_6H_4Ph$,

colourless leaflets, m. p. 133—134°, and 2:4-*dimethoxybenzoyl-phenylethylene oxide*, $\overset{O}{\underset{CHPh}{\bigg>}}CH \cdot CO \cdot C_6H_3(OMe)_2$, colourless

prisms, m. p. 116°, were obtained by the general reaction, using p-chloroacetyldiphenyl and ω-chloro-2:4-dimethoxyacetophenone respectively.

By the action of aluminium chloride on a mixture of chloroacetyl chloride and p-chloroanisole in carbon disulphide, 5-ω-*di-chloro-2-methoxyacetophenone*, colourless leaflets, m. p. 91° (compare Kunckell, A., 1898, i, 254), was formed, together with a small quantity of a *substance* crystallising in needles; the former reacted with benzaldehyde and sodium ethoxide, with formation of 5-*chloro-2-methoxybenzoylphenylethylene oxide*,

$$\overset{O}{\underset{CHPh}{\bigg>}}CH \cdot CO \cdot C_6H_3Cl \cdot OMe,$$
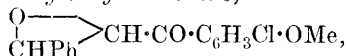
colourless leaflets, m. p. 157°.

5-*Acetylamino-o-toluoylphenylethylene oxide*,

$$\overset{O}{\underset{CHPh}{\bigg>}}CH \cdot CO \cdot C_6H_3Me \cdot NHAc,$$
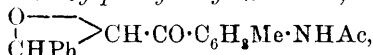
colourless needles, m. p. 149°, was obtained from ω-chloro-5-acetyl-amino-2-methylacetophenone in the general manner; it reacted with alcoholic sodium hydroxide, producing 5-*acetylamino-o-tolyl* α-*hydroxystyryl ketone*, $CHPh \colon C(OH) \cdot CO \cdot C_6H_3Me \cdot NHAc$, prisms, m. p. 130—131°, from which 3(5′-*acetylaminotolyl*)-2-*benzylquin-oxaline*, $C_{24}H_{21}ON_3$, m. p. 124—125°, was obtained. The isomeric 6-*acetylamino*-m-*toluoylphenylethylene oxide*, colourless needles, m. p. 140°, obtained in a similar manner, underwent an unexpected reaction when treated with alcoholic sodium hydroxide solution, the primarily resulting α-diketone immediately losing a molecule of acetic acid, with formation of 3-*keto*-2-*benzylidene*-5-*methyl*-2:3-*dihydroindole*, $C_6H_3Me \overset{NH}{\underset{CO}{<}} > C \colon CHPh$, orange-red leaflets, m. p. 197°. 3-*Acetylamino*-p-*toluoylphenylethylene oxide*, colourless needles, m. p. 152°, and p-*acetylaminobenzoylphenylethylene oxide*,

$$\overset{O}{\underset{CHPh}{\bigg>}}CH \cdot CO \cdot C_6H_4 \cdot NHAc,$$
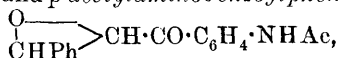
colourless leaflets, m. p. 157°, were prepared by means of the general process; the latter was converted by alcoholic sodium hydroxide into p-*acetylaminophenyl* α-*hydroxystyryl ketone*, $C_{17}H_{15}O_3N$, pale yellow prisms, m. p. 125—126°, which with o-*phenylenediamine*

yielded a 3-p-*acetylaminophenyl-2-benzylquinoxaline*, $C_{28}H_{19}ON_3$, colourless needles, m. p. 199°, and with alcoholic hydrogen chloride gave β-*chloro-γ-keto-α-hydroxy-α-phenyl-γ-p-acetylaminophenyl-propane*, $NHAc·C_6H_4·CO·CHCl·CHPh·OH$, colourless leaflets, m. p. 206° (decomp.); this was easily recovered into the cyclic oxide by sodium ethoxide in alcoholic solution.

p-*Aminobenzoylphenylethylene oxide*, $\overset{O---}{\underset{CHPh}{|}}{>}CH·CO·C_6H_4·NH_2$,

was obtained in colourless leaflets, m. p. 119°. ω-Bromo-*m*-nitro-acetophenone, ω-chloro-5-nitro-4-acetylaminoacetophenone, bischloro-acetylanisole, acetyl-6-chloroacetyltetrahydroquinoline, and chloro-acetone when submitted to treatment with benzaldehyde and alcoholic sodium ethoxide yielded only uncrystallisable products.

D. F. T.

Anthraquinonethioxanthone. FRITZ ULLMANN (*Ber.*, 1917, **50**, 1526).—A claim for priority against Schaarschmidt (A., 1917, i, 703). D. F. T.

Complete Synthesis of Fenchone. L. RUZIČKA (*Ber.*, 1917, **50**, 1362—1374).—As fenchone yields such remarkably labile and somewhat obscure degradation products, it seems to be worthless to attempt to establish its formula except by a direct synthesis.

According to Semmler's formula (annexed) for fenchone, this ketone is α-methylcamphenilone. Just as lead camphenate yields camphenilone on distillation (Komppa, A., 1914, i, 556, 852), so the corresponding salt of homofenchonic acid might be expected to give fenchone. This acid has now been synthesised, but the lead salt gives a mixture of hydrocarbons on distillation, and it is doubtful whether fenchone is present in the product. It appears that the assembling of so many methyl radicles near the carboxyl group hinders the ring closure, for lead camphenate itself only gives a poor yield of camphenilone, whilst lead homo*apo*camphorate produces a fairly large amount of *apo*camphor (*ibid.*, 556).

$$CH_2·CMe·CO$$
$$|\quad CH_2\quad |$$
$$CH_2·CH--CMe_2$$

Methyl*nor*camphor has been synthesised by methods commonly employed in this field, and by a double methylation converted into *dl*-fenchone. Semmler's formula is thus fully established.

Ethyl lævulate is condensed with ethyl bromoacetate under the influence of zinc, and the lactonic ester,

$$\underset{O------CO}{CO_2Et·CH_2·CMe·CH_2·CH_2},$$
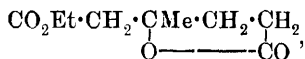
so formed (Duden, A., 1903, i, 400) is heated at 240—250° with potassium cyanide, and so converted into *ethyl β-cyano-β-methyl-butane-αδ-dicarboxylate* (I), a limpid, mobile oil, b. p. 179—180°/13 mm. The crude dicarboxylate is hydrolysed by warming with

concentrated sulphuric acid and alcohol to *ethyl β-methylbutane-αβδ-tricarboxylate* (II), a mobile oil, b. p. 175—178°/12 mm.

$$\begin{array}{ccc} \text{CN·CMe·CH}_2\text{·CH}_2\text{·CO}_2\text{Et} & & \text{CO}_2\text{Et·CMe·C}_2\text{H}_4\text{·CO}_2\text{Et} \\ \text{CH}_2\text{·CO}_2\text{Et} & \longrightarrow & \text{CH}_2\text{·CO}_2\text{Et} \\ \text{(I.)} & & \text{(II.)} \end{array}$$
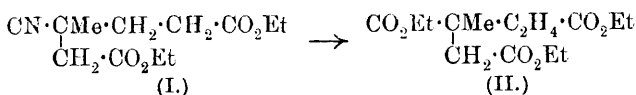
The tricarboxylate is heated with sodium and benzene, and so condensed to 1-*methyl*cyclo*pentan-3-one-1-carboxylic acid*, a viscous oil, b. p. 170°/12 mm., which forms a *semicarbazone*, m. p. 189—190° (decomp.). The *ethyl* ester (III), b. p. 115°/12 mm., is condensed with ethyl α-bromoisobutyrate in the presence of zinc, yielding *ethyl* 3-*hydroxy-3-β-carbethoxyisopropyl-1-methyl*cyclo*pentane-1-carboxylate (ethyl hydroxyhomofenchonate)* (IV), b. p. 171—173°/12 mm.

$$\text{CO}_2\text{Et·CMe}\Big\langle\begin{array}{c}\text{CH}_2\text{·CO}\\\text{CH}_2\text{·CH}_2\end{array} \longrightarrow \text{CO}_2\text{Et·CMe}\Big\langle\begin{array}{c}\text{CH}_2\text{·C(OH)·CMe}_2\text{·CO}_2\text{Et}\\\text{CH}_2\text{·CH}_2\end{array}$$

$$\begin{array}{ccc} \text{(III.)} & & \text{(IV.)} \end{array}$$
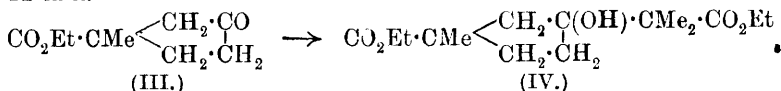
This ester is heated with phosphorus tribromide, when water is eliminated and *ethyl dehydrohomofenchonate*, b. p. 152—153°/12 mm., produced. This yields a mixture of *acids*, $C_{11}H_{16}O_4$, on hydrolysis, minute needles, m. p. 176—177°, and compact crystals, m. p. 110—111°. The ester is reduced by means of hydrogen in the presence of spongy platinum and acetic acid to *ethyl homofenchonate*, b. p. 150—155°/13 mm. *Homofenchonic acid*,

$$\text{CO}_2\text{H·CMe}\Big\langle\begin{array}{c}\text{CH}_2\text{·CH·CMe}_2\text{·CO}_2\text{H}\\\text{CH}_2\text{·CH}_2\end{array}$$
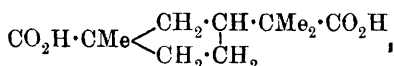
separates from water in minute crystals, m. p. 167—168°.

Ethyl 1-methyl*cyclo*pentan-3-one-1-carboxylate (III) is condensed with ethyl bromoacetate in the presence of zinc and a trace of iodine to form a mixture of the two esters, V and VI.

$$\text{CO}_2\text{Et·CMe}\Big\langle\begin{array}{c}\text{CH}_2\text{·C(OH)·CH}_2\text{·CO}_2\text{Et}\\\text{CH}_2\text{·CH}_2\end{array}$$

$$\text{(V.)}$$

$$\text{CO}_2\text{Et·CMe}\Big\langle\begin{array}{c}\text{CH}_2\text{·C:CH·CO}_2\text{Et}\\\text{CH}_2\text{·CH}_2\end{array}$$

$$\text{(VI.)}$$
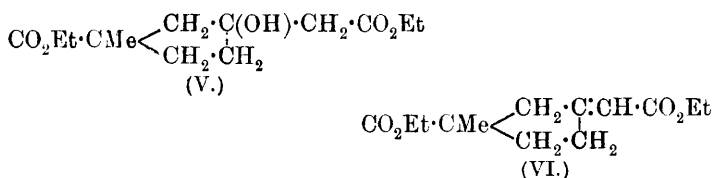
The mixture is completely dehydrated by shaking with phosphorus tribromide in chloroform, and then the *ester* (VI), m. p. 148—152°/15 mm., is reduced as above to *ethyl methyl*norhomocamphorate, b. p. 147—149°/14 mm. The free *acid* (3-*carboxymethyl-1-methyl*cyclo*pentane-1-carboxylic acid*) has m. p. 116—118°, and its lead salt breaks down on distillation in a current of carbon dioxide into *methyl*norcamphor (VII), which is a mobile oil, b. p. 60—62°/15 mm., with camphor-like odour (*semicarbazone*, m. p. 210—211°). This is methylated by means of sodamide and methyl

iodide, and so converted into a mixture of fenchosantenone (VIII)
and *dl* fenchone.

$$
\begin{array}{cc}
\text{CH}_2\cdot\text{CMe}\cdot\text{CO} & \text{CH}_2\cdot\text{CMe}\cdot\text{CO} \\
|\quad\ \ \text{CH}_2\ \ | & |\quad\ \ \text{CH}_2\ \ | \\
\text{CH}_2\cdot\text{CH--CH}_2 & \text{CH}_2\cdot\text{CH--CHMe} \\
\text{(VII.)} & \text{(VIII.)}
\end{array}
$$
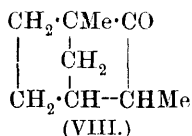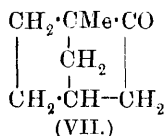
These can be separated by reason of the fact that fenchone does
not readily form a semicarbazone, the method being the one used
by Wallach to separate camphor and fenchone (A., 1907, i, 616).
Fenchosantenone *semicarbazone* forms glistening needles, m. p.
208—209°, and the *oxime* has m. p. 98—99°. The *dl*-fenchone
obtained had b. p. 72—73°/12 mm., and its oxime had the correct
m. p., 158—159°.

It is suggested that the same general plan might be followed in
the synthesis of camphor and *iso*fenchone.   J. C. W.

**Synthesis by means of Sodamide. Preparation of the
Mono- and Di-methylcamphors, of Dimethylcampholamide,
and of Dimethylcampholic Acid.** A. HALLER and ED. BAUER
(*Ann. Chim.*, 1917, [ix], **8**, 117—145).—When camphor (1 mol.)
is boiled in anhydrous benzene with one-quarter of its weight of
sodamide until all action ceases, and then methyl iodide (1 mol.)
is gradually added, and the whole process repeated, a mixture of
methylcamphor and dimethylcamphor is obtained, which can be
separated by converting the methylcamphor into its oxime and
fractionally distilling the mixture. *Dimethylcamphor* is obtained
as a colourless, mobile liquid, b. p. 106°/11 mm., D_4^{25} 0·94708,
n_a 1·46940, n_D 1·47187, n_β 1·47793, n_γ 1·48289, $[\alpha]_D^{25}$ +97°50′, and
in alcoholic solution +92°27′. By the action of sodium in abso-
lute alcohol, it is converted into a mixture of α-*dimethylcamphol*,
m. p. 56—57°, $[\alpha]_D^{25}$ +55°4′ (in alcohol) and $[\alpha]_D^{20}$ +60°4′ (in
benzene), and β-*dimethylcamphol*, which is not obtained entirely
free from its stereoisomeride. The mixed camphols give a *phenyl-
urethane*, m. p. 111·5—112°, $[\alpha]_D^{21}$ +29·5° (in alcohol). With
sodamide in benzene solution, dimethylcamphor yields *dimethyl-
campholamide*, m. p. 72—73°, b. p. 179—180°/14 mm., $[\alpha]_D^{23}$ 70·8°,
which by the action of sodium nitrite in the presence of sulphuric
acid is converted into *dimethylcampholic acid*, m. p. 73—74°,
$[\alpha]_D^{24}$ 47·4° (in alcohol).

The methylcamphoroxime as isolated has m. p. 60°, b. p.
134—135°/11 mm., $[\alpha]_D^{12}$ +23·15° (compare Glover, T., 1908, **93**,
1285), and is shown to be a mixture of an active and an inactive
form. With phenylcarbimide it gives two isomeric α-*methyl-
camphorcarbanilidoximes*, the one crystallising in prisms, m. p.
112—113°, $[\alpha]_D^{12}$ +24·8° (in alcohol), and the other in needles,
m. p. 113°, and inactive. Methylcamphoroxime when boiled with
hydrochloric acid yields α-*methyl-α-campholenonitrile*, b. p.
105°/15 mm., $[\alpha]_D^{13}$ 53·9° (in alcohol), which when boiled with

alcoholic potassium hydroxide gives *α-methylcampholenamide*, m. p. 91—92°, crystallising with $1H_2O$, and quite inactive, and if the hydrolysis is carried further, *methylcampholenic acid*, m. p. 30°, b. p. 153°/20 mm., which is also inactive, is obtained.

<div align="right">W. G.</div>

Constituents of Essential Oils. Elemol, $C_{15}H_{26}O$. F. W. SEMMLER and FUTUNG LIAO (*Ber.*, 1917, **50**, 1286—1291. Compare A., 1916, i, 492).—A further account of this unicyclic sesquiterpene alcohol.

Pure tetrahydroelemol, obtained from the purest elemol or from its benzoate, has m. p. 35·5°, b. p. 138—142°/13 mm., D^{20} 0·9080, n_D 1·4807, a_D −2°. It forms a *benzoate*, b. p. 210—215°/13 mm., D^{20} 0·9927, n_D 1·5092, a_D −8°, and an *acetate*, b. p. 152—155°/12 mm., D^{20} 0·9304, n_D 1·4641, a_D +2°. From the purified oil, a specimen of tetrahydroelemene with b. p. 118—120°/12 mm., D^{20} 0·8576, n_D 1·4760, a_D −15·2°, was obtained by treatment with formic acid.

In order to elucidate the constitution of elemol, the ozonisation of tetrahydroelemene, as the most suitable material, has been investigated. The important products, after decomposing the ozonides, are a *keto-aldehyde*, $C_{15}H_{28}O_2$, b. p. 140—170°/10 mm., which reacts with semicarbazide to give a complicated mixture, and the corresponding *ketonic acid*, $C_{15}H_{22}O_3$, b. p. 180—205°/10 mm., which forms a *methyl* ester, b. p. 165—170°/10 mm. A considerable yield of the acid is obtained if the ozonisation is prolonged until the yellow colour which develops at first disappears again. The keto-acid gives a *dicarboxylic acid*, $C_{12}H_{22}O_4$, b. p. 180—205°/10 mm., when oxidised by a hypobromite solution, which indicates the presence of an *iso*propyl group. Tetrahydroelemene may therefore have the annexed formula, but the position of the side-chain is not yet determined.

CHMe₂
|
C
HC⟋ ⟍CH₂
H₂C⟍ ⟋CH·C₅H₁₁
CHMe
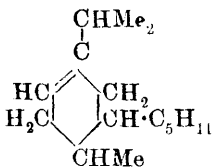
Crude elemol contains small quantities of a more volatile, denser oil, b. p. 135—145°/10 mm., D^{20} 0·9670, n_D 1·5171, a_D −3·6°, which may be a *phenolic ether*,
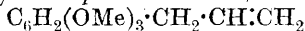
$$C_6H_2(OMe)_3·CH_2·CH:CH_2$$

or $C_6H_2(OMe)_3·CH_2·CH:CHMe$, for it may be oxidised to an *acid*, $C_6H_2(OMe)_3·CH_2·CO_2H$, m. p. 185—186°.

<div align="right">J. C. W.</div>

The Colloidal Nature of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 115—124).—The nature of colophony is discussed in reference to the various products which are obtained by the action of acids on its solutions in alkalis. The chief substance is γ-pinic acid, m. p. 75—76°, which contains a maximum amount of combined water in a colloidal form. By the action of dehydrating agents, sylvic acid and "Malysäure" are formed as intermediate products, the final product of the dehydration process

being γ-abietic acid, m. p. 161—163°. These substances form a series which offers some resemblance to the silicic acids commencing with colloidal silicic acid and ending with silica.

Hydrocarbons and ethers behave similarly to water, and enter into combination with colophony in colloidal form. The solid colloidal solutions which are thereby formed represent a new and distinct type from the point of view of the colloid chemist, and commercial colophony is to be regarded as belonging to this group.

H. M. D.

Bixin. A. HEIDUSCHKA and A. PANZER (*Ber.*, 1917, **50**, 1525—1526).—A reply to Herzig and Faltis (A., 1917, i, 577) maintaining the probability of the formula $C_{25}H_{30}O_4$ for bixin.

D. F. T.

3 : 4-Di-*p*-nitrotetraphenylfuran. ARTHUR GORDON FRANCIS (T., 1917, **111**, 1039—1043).—When *p*-nitroacetylbenzoin and *p*-nitrobenzoylbenzoin are hydrolysed by means of alcoholic hydrogen chloride, they yield *p*-nitrobenzil and 3 : 4-*di*-p-*nitrotetraphenylfuran*. The reaction is supposed to proceed as follows. First, the acyl compound is hydrolysed to *p*-nitrobenzoin; two molecules of this condense together, and the product is reduced to dinitrobidesyl at the expense of a third molecule, which is oxidised to p-nitrobenzil, thus :

$$3NO_2 \cdot C_6H_4 \cdot CHBz \cdot OH = NO_2 \cdot C_6H_4 \cdot CHBz \cdot CHBz \cdot C_6H_4 \cdot NO_2 + NO_2 \cdot C_6H_4 \cdot COBz,$$
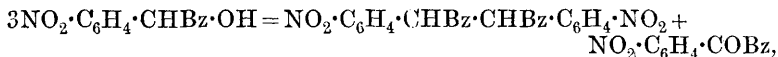
and, finally, the dinitrobidesyl suffers loss of water and changes into the furan, $O{<}^{CPh:C \cdot C_6H_4 \cdot NO_2}_{CPh:C \cdot C_6H_4 \cdot NO_2}$. The intermediate products have not been isolated, but analogous compounds in the case of benzoin itself are well known.

For experimental details, see the original. J. C. W.

Formation of Halogenated Chromones [γ-Benzopyrones]. H. SIMONIS and HANS SCHUHMANN (*Ber.*, 1917, **50**, 1142—1149).—It was recently shown that, by vigorous methods, bromine can be introduced into the methyl groups of 2 : 3-dimethylchromone, but that the benzene nucleus is only affected under extreme conditions (A., 1917, i, 408). Chromones containing halogens in the benzene nucleus can, however, be obtained readily by the condensation of halogenophenols with alkylacetoacetic esters under the influence of phosphoric oxide (compare A., 1913, i, 890). On the other hand, halogen atoms in the ester component hinder the condensation with phenols, and chromones substituted in the pyrone nucleus cannot be obtained by this method.

p-Chlorophenol and ethyl methylacetoacetate yield 6-*chloro*-2 : 3-*dimethyl-γ-benzopyrone*, in long needles, m. p. 107°. This forms an *oxime*, m. p. 202°, reacts with phosphorus pentasulphide at

120° to give 6-*chloro-2 : 3-dimethyl-γ-benzothiopyrone* (annexed formula), red needles, m. p. 142·5°, and is hydrolysed by boiling, dilute sodium hydroxide to 5-chlorosalicylic acid. 6-*Chloro-2-methyl-3-ethyl-γ-benzopyrone,* needles, m. p. 109°, from ethyl ethylacetoacetate, forms an *oxime,* m. p. 165·5°, and a *compound* with $1HgCl_2$, which crystallises in needles, often an inch long.

p-Bromophenol gives rise to 6-*bromo-2 : 3-dimethyl-γ-benzopyrone,* which crystallises in very long prisms, m. p. 111—112°, and 6-*bromo-2-methyl-3-ethyl-γ-benzopyrone,* long needles, m. p. 190°.

o-Chlorophenol yields 8-*chloro-2 : 3-dimethyl-γ-benzopyrone,* pale yellow leaflets, m. p. 108°, and 8-*chloro-2-methyl-3-ethyl-γ-benzopyrone,* long spikes, m. p. 85°, which forms a *compound* with $1HgCl_2$, pale yellow columns, m. p. 134°.

o-Bromophenol gives 8-*bromo-2 : 3-dimethyl-γ-benzopyrone,* needles, m. p. 108°, which yields 3-bromosalicylic acid, m. p 183—184°, on hydrolysis, and 8-*bromo-2-methyl-3-ethyl-γ-benzopyrone,* prisms, m. p. 94°.

m-Halogenophenols can theoretically give 5- and 7-halogenoderivatives. As usual, their constitutions are best revealed by identifying the halogeno-salicyclic acids or other products which they yield on hydrolysis. *m*-Chlorophenol and ethyl dimethylacetoacetate give a mixture from which 7-*chloro-2 : 3-dimethyl-γ-benzopyrone,* m. p. 155°, can be isolated; this yields 4-chlorosalicylic acid on hydrolysis. *m*-Bromophenol, on one occasion, gave 5-*bromo-2 : 3-dimethyl-γ-benzopyrone,* m. p. 163°, only, but usually the 7-*bromo*-compound, m. p. 108—110°, is formed as well. It has already been shown that the former yields 6-bromo-2-hydroxyphenyl ethyl ketone on hydrolysis, and the latter 4-bromosalicylic acid (A., 1917, i, 580). Individual compounds are usually given by ethyl ethylacetoacetate, but their constitutions have not been determined. 5- or 7-*Chloro-2-methyl-3-ethyl-γ-benzopyrone* has m. p. 133°, and the 5- or 7-*bromo*-compound has m. p. 137°.

2 : 4-Dihalogenophenols react to form the 6 : 8-dihalogenochromones, but the condensation does not take place so readily. 6 : 8-*Dichloro-2 : 3-dimethyl-γ-benzopyrone* has m. p. 141°, the 6 : 8-*dibromo*-compound has m. p. 128·5°, and 6 : 8-*dichloro-2-methyl-3-ethyl-γ-benzopyrone* has m. p. 105°. J. C. W.

Further Investigations on the Formation and Opening of the Coumaranone Ring. K. von Auwers and W. Müller (*Ber.,* 1917, **50**, 1149—1177. Compare A., 1914, i, 981, 1136; 1915, i. 440; 1916, i, 496; 1917, i, 277).—It has been shown that 1 : 4-dimethylcoumaran-2-one readily changes into 4-acetoxy-*m*-toluic acid on exposure to the air. The rupture of the heterocyclic system between positions 1 and 2 during auto-oxidation is not exhibited to such a remarkable degree by other alkylcoumaranones, and no conclusions as to the connexion between structure and reactivity in this sense can safely be drawn.

The coumaranone ring can often be opened, however, between the oxygen atom and carbon atom 1, by means of the ketone reagents, semicarbazide (A., 1915, i, 440), hydroxylamine, o-phenylenediamine, and some phenylhydrazines. The behaviour of various coumaranones towards these reagents has therefore been examined, in order to determine, if possible, the influence of substituents on the stability of the ring. It is found, as before, that substituents in the benzene nucleus in the ortho- or para-positions with regard to the oxygen atom generally tend to weaken the ring, whilst meta-substituents have a stabilising effect.

Conversely, the ease with which o-α-halogenoacylphenols undergo ring closure to coumaranones when treated with alkali hydroxides has been examined. Extreme cases are represented by 6-chloro-acetyl-5-m-xylenol, which changes with the greatest ease into 3 : 5-dimethylcoumaranone, and m-α-bromoisobutyryl-p-cresol, which yields either m-α-hydroxyisobutyryl-p-cresol or 3 : 6-dimethyl-1 : 4-benzopyrone, but no coumaranone at all. Many intermediate cases are now described in which both reactions take place, but it is evident that meta-substituents with regard to the hydroxyl group favour the formation of coumaranones, and that methoxyl is more active in this respect than methyl.

1 : 4-DIMETHYLCOUMARANONE SERIES.—1 : 4-Dimethylcoumaranone does not react with o-phenylenediamine, but 1-hydroxy-1 : 4-dimethylcoumaran-2-one condenses with this agent in boiling acetic acid to form 2-4'-*hydroxy*-m-*tolyl*-3-*methylquinoxaline*, thus :
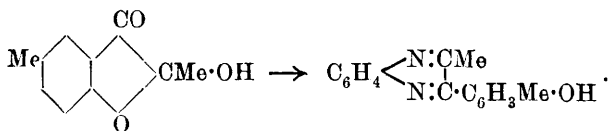
This compound crystallises in large, glistening prisms, m. p. 194—195°, and reacts with methyl sulphate to form a *methyl ether*, silky needles, m. p. 96—97°, which may also be prepared by condensing o-phenylenediamine with 4-methoxy-m-tolyl methyl diketone, $OMe \cdot C_6H_3Me \cdot CO \cdot COMe$ (A., 1915, i, 440).

3-α-Chloropropionyl-p-cresol dissolves in 2N-sodium hydroxide with golden-yellow colour, giving chiefly the coumaranone derivative, but also some α-hydroxypropionylcresol. These were not isolated as such, but converted into methyl ethers by means of methyl sulphate, and then separated by distillation. 2-*Methoxy*-1 : 4-*dimethylcoumarone*, $C_6H_3Me{<}^{C(OMe)}_{O}{>}CMe$, distils, first, as a colourless, pleasant-smelling oil, b. p. 126—126·5°/19 mm., D_4^{20} 1·081, n_D^{20} 1·5451, $E\Sigma_r + 0·77$, $E\Sigma_D + 0·85$, $E\Sigma_\beta - \Sigma_\alpha + 55\%$, $E\Sigma_\gamma - \Sigma_\alpha + 64\%$ (average values). The same compound is obtained by shaking an alkaline solution of 1 : 4-dimethylcoumaranone with methyl sulphate. The liquid with higher b. p. is m-*lactyl*-p-*methoxytoluene*, $OMe \cdot C_6H_3Me \cdot CO \cdot CHMe \cdot OH$, and is a pale yellow oil, b. p. 154—156°/16 mm., D_4^{20} 1·099, n_D^{20} 1·5259, $E\Sigma_a + 0·81$,

$E\Sigma_D + 0.85$, $E\Sigma_\beta - \Sigma_a + 44\%$. The same oil was synthesised as follows: *m*-propionyl-*p*-methoxytoluene is brominated, the *m*-α-bromopropionyl compound (b. p. 161–163°/14 mm.) is boiled with potassium acetate in dry alcohol, and the m-α-*acetoxypropionyl*-p-*methoxytoluene* (glassy needles, m. p. 70–71°) is hydrolysed.

4-Methyl-1-ethylcoumaranone Series.—3-α-*Chlorobutyryl*-p-*cresol* is prepared by the condensation of α-bromobutyryl bromide with *p*-cresol methyl ether under the influence of aluminium chloride. It crystallises in stout, glassy prisms, m. p. 61—62°, b. p. 159—160°/12 mm., and condenses, under the influence of sodium acetate or hydroxide, to 4-*methyl-1-ethylcoumaran-2-one*. This crystallises in long, flat, glassy prisms, m. p. 41°, b. p. 140–142°/14 mm., and has a sweet odour. The *acetate* (of the enolic form) is a highly refractive oil, b. p. 160–161°/13 mm., which is immediately hydrolysed by alkali hydroxides. It behaves like 1:4-dimethylcoumaranone towards semicarbazide, forming a normal *semicarbazone*, $C_{12}H_{15}O_2N_3$, glassy needles, m. p. 195°, which is insoluble in sodium hydroxide, and then suffering rupture of the ring, with the production of the *compound*,

$$OH \cdot C_6H_3Me \cdot C(:N \cdot NH \cdot CO \cdot NH_2) \cdot CHEt \cdot NH \cdot NH \cdot CO \cdot NH_2,$$

or the true disemicarbazone,

$$OH \cdot C_6H_3Me \cdot C(:N \cdot NH \cdot CO \cdot NH_2) \cdot CEt:N \cdot NH \cdot CO \cdot NH_2.$$

This is soluble in alkali hydroxides, forms slender needles, m. p. 223—224°, and is hydrolysed by hydrochloric acid to 1-*hydroxy-4-methyl-1-ethylcoumaran-2-one*, which crystallises in glistening needles, m. p. 95—96°. The latter compound is more easily prepared by the action of sodium carbonate on 1-*bromo-4-methyl-1-ethylcoumaran-2-one*, which is obtained in silky needles, m. p. 44—45°, by brominating 4-methyl-1-ethylcoumaranone.

4-Methyl-1-*iso*propylcoumaranone Series.—3-α-*Chloro*isovaleryl-p-*cresol*, from α-bromo*iso*valeryl bromide, *p*-cresol methyl ether, and aluminium chloride, crystallises in glistening, yellow needles, m. p. 75—76°, and is readily converted, as above, into 4-*methyl-1-iso*propylcoumaran-2-one. This crystallises in long prisms, m. p. 25—26.5°, b. p. 147—148°/16 mm., and forms an *acetate*, b. p. 162—163.5°/13 mm. It is very stable towards semicarbazide, and even the *semicarbazone*, m. p. 170—171°, is only produced in a small yield. The *oxime*, glistening, slender needles, m. p. 142—143°, is more readily formed, but an excess of hydroxylamine does not bring about rupture of the ring. 1-*Bromo-4-methyl-1-iso*propylcoumaran-2-one, silky needles, m. p. 65.5—66.5°, is obtained by direct bromination, and converted, as above, into the 1-*hydroxy*-compound, felted needles, m. p. 118—119°. This is stable towards semicarbazide, but reacts with *o*-phenylenediamine to give 2-4'-*hydroxy*-m-*tolyl*-3-iso*propylquinoxaline*,

$$C_6H_4 \!\!<\!\! \begin{matrix} N:CPr^3 \\ N:C \cdot C_6H_3Me \cdot OH \end{matrix}'$$
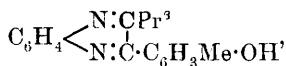
m. p. 161—162°.

1:3:5-TRIMETHYLCOUMARANONE SERIES.—The methyl ether of *s.-m*-xylenol and α-bromopropionyl bromide condense together, under the influence of aluminium chloride, to give a mixture containing 60—70% of the coumaranone directly. Any of the normal chloro-ketone in the mixture is readily transformed into the coumaranone by means of sodium hydroxide. 1:3:5-*Trimethylcoumaran-2-one* forms large, transparent crystals, m. p. 25—27°, b. p. 142·5—143°/14 mm., yields an *acetate*, long, glassy needles, m. p. 60—61°, b. p. 163·5—164/14 mm., and gives a very poor yield of a *semicarbazone*, m. p. 231—232°. 1-*Hydroxy*-1:3:5-*trimethylcoumaran-2-one* is obtained through the 1-bromo-derivative, in glistening needles, m. p. 115—117°.

5-METHOXY-1-METHYLCOUMARANONE SERIES.—Resorcinol dimethyl ether and α-bromopropionyl bromide are condensed together, under the influence of aluminium chloride, to form 6-α-*chloropropionyl-3-methoxyphenol*, stout, yellow, glassy prisms, m. p. 84—85°, and this is converted into 5-*methoxy-1-methylcoumaran-2-one*, which crystallises in long, glistening needles, m. p. 60—61°. Semicarbazide reacts with this ketone to form the *semicarbazone*, m. p. 194—195°, and after a time the *disemicarbazone*, $C_{12}H_{16}O_4N_6$, m. p. 235—236°, of the opened, unicyclic compound. 1-*Bromo-5-methoxy-1-methylcoumaran-2-one* forms bundles of silky needles, m. p. 74—75°, and the 1-*hydroxy*-compound, which may be obtained from the bromo-derivative, or by boiling the above disemicarbazone with dilute hydrochloric acid, crystallises in glistening prisms, m. p. 115—116°.

4-METHOXY-1-METHYLCOUMARANONE SERIES.—Quinol dimethyl ether and α-bromopropionyl bromide give rise to 4-*methoxy-2-α-chloropropionylphenol*, which crystallises in deep yellow needles, m. p. 47—49°, b. p. 181—183°/13 mm., and may be converted into 2-*propionyl-4-methoxyphenol* (long, glassy needles, m. p. 47—49°, b. p. 158—160°/19 mm.) by the action of zinc and acetic acid. The chloroketone reacts with sodium acetate to give a yellow oil which is apparently a mixture of 4-methoxy-1-methylcoumaranone and unicyclic hydroxy-ketone. The mixture reacts most readily with semicarbazide to form the *disemicarbazone*,

$$OMe \cdot C_6H_3(OH) \cdot C \Big\langle \begin{matrix} N \cdot NH \cdot CO \cdot NH_2 \\ CMe : N \cdot NH \cdot CO \cdot NH_2 \end{matrix} \Big. ,$$

m. p. 207—208°. No trace of a coumaranone semicarbazone can be found. The crude chloroketone behaves similarly with sodium hydroxide, and in this case it is possible to methylate the product, and so to isolate 2:4-*dimethoxy-1-methylcoumarone*,

$$OMe \cdot C_6H_3 \Big\langle \begin{matrix} C(OMe) \\ O \end{matrix} \Big\rangle CMe,$$
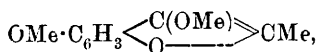
b. p. 150—150·5°/15 mm., D_4^{20} 1·444, n_D^{20} 1·5520, $E\Sigma_\alpha$ + 0 94°, $E\Sigma_D$ + 1·02, $E\Sigma_\beta - \Sigma_\alpha + 65\%$, $E\Sigma_\gamma - \Sigma_\alpha + 77\%$, and 2-*lactyl*-1:4-*dimethoxybenzene*, $C_6H_3(OMe)_2 \cdot CO \cdot CHMe \cdot OH$, b. p. 172—175°/15 mm., D_4^{20} 1·142, n_D^{20} 1·5323, $E\Sigma_\alpha$ + 1·26, $E\Sigma_D$ + 1·31, $E\Sigma_\beta - \Sigma_\alpha +$ 60%.   J. C. W.

Hydroxycoumaranones. ADOLF SONN (*Ber.*, 1917, **50,** 1262—1270).—The most suitable method for the preparation of hydroxycoumaranones seems to be to bring about internal condensation in *o*-chloroacetyl derivatives of the polyhydric phenols, as, for example, in the formation of 5:6-dihydroxycoumaranone ("anhydroglycogallol") from 6-chloroacetylpyrogallol,
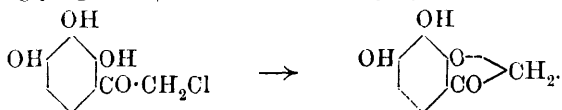
The usual methods for the preparation of the chloroacetyl derivatives are of very limited application, and leave much to be desired, but they can be obtained most readily from chloroacetonitrile and the phenols by Hoesch's new ketone synthesis (A., 1915, i, 820).

An ethereal solution of phloroglucinol and chloroacetonitrile is saturated with hydrogen chloride, when the hydrochloride of the keto-imide, $C_6H_2(OH)_3 \cdot C(CH_2Cl){:}NH,HCl$, is precipitated. This is hydrolysed, as usual, by boiling with water, but the chloroacetylphloroglucinol almost entirely changes into the coumaranone during the same operation. The condensation is completed by adding a little chalk or potassium acetate to the water. 3:5-*Dihydroxycoumaranone* forms stout, glassy tablets, m. p. 250° (decomp.), and yields a *diacetate*, glistening, hexagonal prisms, m. p. 122°, and a 1-*anisylidene* compound, stellate bundles of orange-yellow needles, m. p. 224—225°.

An excellent yield of 6-*chloroacetylresorcinol* can be obtained by the same method. The ketone crystallises in stout prisms or thick bundles of slender needles, m. p. 131°, and reacts with diazomethane to form 3-methoxy-6-chloroacetylphenol (ω-chloro-2-hydroxy-4-methoxyacetophenone; Auwers and Pohl, A., 1914, i, 981), from which 5-methoxycoumaranone (*ibid.*) is readily obtained. It is also converted into 5-*hydroxycoumaranone* (Brüll and Friedländer's *m*-hydroxyketocoumaran, A., 1897, i, 221) by boiling with alcohol and potassium acetate. This compound crystallises in pearly leaflets, m. p. 242°, and reacts with acetic anhydride to form a mono-acetate, pearly scales, m. p. 79° (*ibid.*), and a *diacetyl* derivative, stout crystals, m. p. 157—159°.

J. C. W.

4-Hydroxycoumarins. ADOLF SONN (*Ber.*, 1917, **50,** 1292—1305).—Some applications of Hoesch's method (A., 1915, i, 820; 1917, i, 342) to the production of 4-hydroxycoumarins are described.

Phloroglucinol and malononitrile are condensed together by means of hydrogen chloride, and the intermediate imide hydrochloride is boiled with water, when o-*cyanoacetylphloroglucinol*, $CN \cdot CH_2 \cdot CO \cdot C_6H_2(OH)_3$, m. p. 260° (decomp.), together with 2:4:6:2′:4′:6′-*hexahydroxydibenzoylmethane*, elongated tablets, which blacken at 300°, are produced. The cyanoacetylphloroglucinol changes into 4:5:7-trihydroxycoumarin (below) when boiled with dilute acids. Resorcinol behaves in a similar manner,

yielding 6-cyanoacetylresorcinol, nodules of needles, m. p. 270—272° (decomp.), which changes into 4 : 7 dihydroxycoumarin (below) on hydrolysis.

Instead of using malononitrile in the above syntheses, cyano-acetic acid may be employed. This gives stable 4-imino-compounds of the coumarins, which can be converted into acetyl and methoxyl derivatives or hydrolysed by means of 50% sulphuric acid to the 4-hydroxycoumarins.

Resorcinol, cyanoacetic acid, and zinc chloride are mixed in ether and saturated with hydrogen chloride, when *4-imino-7-hydroxy-3 : 4-dihydro-1 : 2-benzopyrone* (annexed formula) is obtained. This crystallises from about 65% acetic acid, has m. p. 340° (decomp.), dissolves in dilute potassium hydroxide with bluish-violet fluorescence, and can be recovered unchanged, and forms a characteristic *diacetyl* compound, glistening needles, m. p. 251°, which changes into a *monoacetyl* derivative (hydroxyl group open?), m. p. 295° (decomp.), when dissolved in dilute alkali hydroxide. The compound may also be converted into the *7-methoxy*-derivative by means of methyl sulphate; this crystallises from acetic acid in heavy, glistening, hexagonal columns, m. p. 300° (decomp.), and forms an *acetyl* compound, m. p. 295° (decomp.). The imide is hydrolysed, as mentioned above, to *4 : 7-dihydroxycoumarin* (*7-hydroxy-4-keto-3 : 4-dihydro-1 : 2-benzopyrone*) (annexed formula). This crystallises from water in long, silky needles, $2H_2O$, m. p. 265° (decomp.), and forms a *diacetate*, which changes into the *7-acetyl* compound, m. p. 223°, when distilled with steam. It also yields *4 : 7-dimethoxycoumarin*, long, slender needles, m. p. 156°, and the *7-methoxy*-derivative,
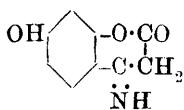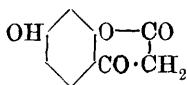
$$OMe \cdot C_6H_3 \overset{O-CO}{\underset{CO \cdot CH_2}{<}},$$
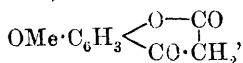
long, pliable needles, m. p. 256° (decomp.), when treated with methyl sulphate; the latter is soluble in alkali hydroxides. The compound also condenses with aldehydes under the influence of hydrochloric acid, and forms a 3-oximino-derivative.

Phloroglucinol and cyanoacetic acid react in the presence of hydrogen chloride to form *4-imino-5 : 7-dihydroxy-3 : 4-dihydro-1 : 2-benzopyrone*, which crystallises in prismatic needles, m. p. above 300° (decomp.). The compound is sparingly soluble in hot water, but a much more soluble modification is obtained if ethyl cyano-acetate is used instead of the free acid. Both forms yield the same *triacetyl* derivative, long, very thin needles, m. p. 197°, which changes into a *diacetyl* compound, m. p. 300° (decomp.), when dissolved in dilute sodium hydroxide. The keto-imide also forms a 5 : 7-*dimethoxy*-compound, stout, double pyramids, m. p. 260° (*acetyl* derivative, m. p. 213°), and may be hydrolysed by dilute sulphuric acid to 4 : 5 : 7-trihydroxycoumarin (5 : 7-dihydr-

oxy-4-keto-3 : 4-dihydro-1 : 2-benzopyrone). This compound has hitherto been obtained by the hydrolysis of Jerdan's lactone (compare Leuchs and Sperling, A., 1915, i, 141), but the present method is much more direct. The anhydrous ketone sinters at 210° and has m. p. above 300° (decomp.). It forms a *triacetate*, m. p. 155—156°, and a *diacetate*, m. p. 210 --211°, and a *3-anisylidene* compound, $C_6H_2(OH)_2 \overset{O-CO}{\underset{CO \cdot C:CH \cdot C_6H_4 \cdot OMe}{<}}$, in delicate, orange-yellow needles, m. p. 256° (decomp.).

Jerdan's lactone, ethyl 4 : 5 : 7-trihydroxycoumarin-8(or 6)-carboxylate (A., 1917, i, 277), forms a *triacetate*, in hard, stout, hexagonal prisms, m. p. 146—147°, which change into Leuchs and Sperling's diacetate, m. p. 196—197°, when treated with cold alkali hydroxide or boiled with water. It also reacts with nitrous acid to give a 3-*oximino*-compound, pale greenish-grey, elongated tablets, m. p. 157° (decomp.). J. C. W.

N-**Methylconiine.** J. von Braun (*Ber.*, 1917, **50**, 1477).—The methylconiine, $[\alpha]_D + 35\cdot66°$, obtained earlier by the author from hemlock (A., 1905, i, 811) was in reality a mixture of *d*- and *l*-methylconiine, the former predominating, and the salts then described were those of the *dl*-base (see also Hess and Eichel, this vol., i, 34). D. F. T.

The Alkaloids of the Pomegranate Tree. III. Constitution of Pelletierine. Kurt Hess and Annaliese Eichel (*Ber.*, 1917, **50**, 1192—1199. Compare A., 1917, i, 349).—Further researches on pelletierine have revealed the interesting fact that the alkaloid is the aldehyde of coniine, or β-2-*piperidylprop-aldehyde.*

Pelletierine yields an *oxime*, b. p. 173°/21 mm., which occurs apparently in two geometric forms, m. p. 96—97° (from light petroleum) and m. p. 80° (from ether), and gives a *picrate*, m. p. 179—180°. When the oxime is treated with phosphorus pentachloride, both dissolved in warm phenetole, it changes into the corresponding *nitrile*, which is a stable, mobile oil, b. p. 104—106°/15 mm., with a pungent, menthol-like odour, and forms a *picrate*, in long needles, m. p. 175—176°. The nitrile may be hydrolysed to the acid and this converted into the ester, which is identical with Löffler and Kaim's ethyl β-2-piperidylpropionate (A., 1909, i, 179). The acid has not yet been obtained by oxidising pelletierine.

Pelletierine *hydrazone* is a limpid syrup, b. p. 150°/20 mm., which is reduced to racemic coniine by heating with sodium ethoxide solution in a sealed tube at 156—170°. The identity of the product is fully established.

Although a secondary base, pelletierine does not react with nitrous acid. This is obviously due to some influence of the aldehyde group on the imino-group. J. C. W.

The Alkaloids of the Pomegranate Tree. IV. A Scheme for the Isolation of the Pure Pelletierine Alkaloids. Determination of the Constitution of Methyl*iso*pelletierine ("Methylpelletierine." "*iso*Methylpelletierine"). Transformation of Conhydrine into Methyl*iso*pelletierine. Constitution of Conhydrine. KURT HESS and ANNALIESE EICHEL (*Ber.*, 1917, **50**, 1386—1407).—In the new investigations of the pelletierine alkaloids, the authors have not encountered optically active bases, and are inclined to doubt whether the active "pelletierine" and "methylpelletierine" described by Tanret were really pure. They have therefore adopted the name "pelletierine" for the inactive base which Tanret designated *iso*pelletierine, and have also shown that Tanret's methylpelletierine and Piccinini's *iso*methylpelletierine are identical. The latter base is not really a methylated pelletierine, but a methyl derivative of an unknown *iso*pelletierine, and therefore the new name methyl*iso*pelletierine is proposed.

Methyl*iso*pelletierine is already known to be a tertiary base with a carbonyl group, and the formula $C_9H_{17}ON$ is well established. It is possible to convert its hydrazone into 1-methylconiine, as pelletierine was transformed into *dl*-coniine (preceding abstract). It may therefore be one of the three bases represented thus:

$$CH_2\begin{matrix}CH_2-CH_2\\CH_2\cdot NMe\end{matrix}CH-CH_2\cdot CH_2\cdot CHO \text{ or } -CH_2\cdot COMe \text{ or } -COEt.$$
$$(A.) \qquad\qquad (B.) \qquad (C)$$
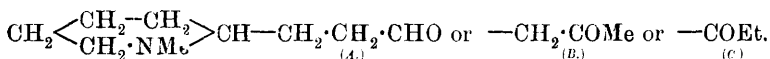
It is not identical with *A*, which is methylpelletierine (A., 1917, i, 350), or with *B*, which is α-1-methylpiperidyl-2-propan-β-one (*ibid.*, 352), and therefore it can only be the compound *C*.

It is an interesting fact that pelletierine and methyl*iso*pelletierine are so closely connected with coniine and 1-methylconiine, two of the hemlock alkaloids. Conhydrine is also nearly related to methyl*iso*pelletierine. Its structure had not been definitely established hitherto, but it can be converted into methyl*iso*pelletierine, and is thus revealed as α-2-piperidylpropyl alcohol.

Attention is directed again to the fact that no optically active modifications of these bases have been found in the pomegranate root. Whilst animals almost exclusively synthesise one active isomeride (except in the case of lactic acid fermentation), the pomegranate, at any rate, produces both forms or is able to bring about racemisation.

After many attempts, it has been found that the best way to separate pelletierine and methyl*iso*pelletierine is to treat the mixture with ethyl chloroformate, when the former, as a secondary base, yields a urethane, whilst the latter, as a tertiary base, remains unchanged, and has a much lower b. p. than the urethane. A new scheme for the isolation of the three alkaloids, crystalline ψ-pelletierine, b. p. 145°/vac., pelletierine, b. p. 106°/21 mm., and methyl*iso*pelletierine, b. p. 114—115°/24 mm., from the root-rind of the pomegranate tree, is now described.

The *urethane* from pelletierine, β-1-*carbethoxypiperidyl-2-prop-*

aldehyde, is a limpid, slightly viscous oil, b. p. 173—174°/20—21 mm., and is readily hydrolysed to pelletierine by heating with concentrated hydrochloric acid at 125—130°.

Methyl*iso*pelletierine *hydrobromide* crystallises in very long needles, m. p. 151—152°, and depresses the m. p. of 1-methyl-pelletierine hydrobromide. The *hydrazone* is a stable, limpid oil, b. p. 154—155°/29 mm., which yields *dl*-1-methylconiine when heated with sodium ethoxide solution at 150—170°. The identity of the base is fully established by means of the usual salts. Although *d*-coniine is rendered almost inactive by heating with barium hydroxide solution and alcohol at 180—230°, it yields a highly active 1-methylconiine when heated with formaldehyde and formic acid at 125—130°. Consequently, a specimen of *dl*-methyl-coniine was obtained for comparative purposes by methylating the *dl*-coniine derived from pelletierine.

Conhydrine, $[\alpha]_D^{20} + 7\cdot12°$, is also methylated by the formaldehyde-formic acid method. 1-*Methylconhydrine* (*α*-1-*methylpiperidyl-2-propyl alcohol*) has b. p. 102—103°/19 mm., and the *sulphate* has $[\alpha]_D^{21} - 20\cdot9°$, in water. When oxidised by chromic acid, it loses the methyl group in addition, and gives *α*-2-*piperidylpropan-α-one* (2-*piperidyl ethyl ketone*), b. p. 94°/18 mm.; the *sulphate* has $[\alpha]_D^{23} - 7\cdot8°$, in water. This behaviour of tertiary 1 : 2-hydroxy-amines may be general, for it has already been observed in the case of *α*-1-methylpyrrolidyl-2-butyl alcohol (A., 1917, i, 353). 2-Piperidyl ethyl ketone cannot be methylated by the formaldehyde method, but methyl sulphate converts it into 1-*methyl-2-piperidyl-ethyl ketone*, which is identical with methyl*iso*pelletierine.

2-*Piperidylacetone* (*α*-2-*piperidylpropane-β-one*) has been prepared by the oxidation of *α*-2-piperidylpropan-β-ol (A., 1916, i, 69); it is a colourless oil, b. p. 108—111°/24 mm., which readily darkens on exposure to air. It yields a *hydrobromide*, m. p. 179°, a *picrate*, m. p. 113—114°, a *semicarbazone hydrochloride*,

$$C_9H_{18}ON_4,HCl,\tfrac{1}{2}H_2O,$$
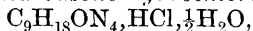
m. p. 164—165° (decomp.), and a *urethane*, m. p. 209°. J. C. W.

Nicotinic Acid Derivatives. I. E. WINTERSTEIN and A. B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1917, **100**, 170—184).—On the reduction of trigonelline with hydrogen in the presence of platinum-black, a *substance* is produced which in some respects closely resembles arecaidine. It gives a crystalline hydrochloride and platinichlorides and aurichlorides which have the same melting points as those recorded for the corresponding arecaidine compounds. The *N*-methyl derivative, prepared by the action of methyl iodide on the reduction product of trigonelline, yields a platinichloride which is identical in melting point and crystalline form with the corresponding salt prepared from arecaidine. On the other hand, the *aurichloride* (short, stout prisms, m. p. 225—230°) and the *picrate* (needles) of the reduction product differ in crystalline form from the similar compounds derived from arecaidine, whilst the mercury salt melts at 205—208° instead of 174—176°. Moreover, the methyl ester of the reduction product,

which should be identical with arecoline, yields a non-crystalline hydrochloride, an *aurichloride*, $C_8H_{13}O_2N,HAuCl_4$, slender needles, m. p. 134—135°, and a *platinichloride*, stout needles, m. p. 192—193°, whilst the corresponding arecoline hydrochloride is a crystalline substance, m. p. 157°, the aurichloride a non-crystalline oil, and the platinichloride crystallises in rhombs, m. p. 176° (decomp.). The authors draw the conclusion that their reduction product from trigonelline is not identical with arecaidine.

When potassium nicotinate is heated at 150° with ethyl iodide and the product shaken with silver chloride, *ethylarecaidine chloride* is formed, needles, m. p. 238°. On reduction, the *chloride* of *ethyltetrahydroarecaidine*, $C_8H_{13}O_2NCl$, is produced, m. p. 230—231°.   H. W. B.

Action of Aldehydes on the Hydramines of the Pyrrolidine and Piperidine Series. VI. Action of Formaldehyde on α-2-Piperidylpropan-β-ol.

Kurt Hess and Annaliese Eichel (*Ber.*, 1917, **50**, 1407—1412. Compare A., 1916, i, 67; 1917, i, 352). —In an earlier paper, it was reported that α-2-piperidylpropan-β-ol is converted into α-1-methyl-2-piperidylpropan-β-one by the action of formaldehyde, but later, when this ketone was prepared by the oxidation of the corresponding secondary alcohol, it was recognised that formaldehyde must have given some other product in the first case. It is now found that the action of formaldehyde on the above secondary alcohol is much more complicated than was imagined.

The base reacts with 40% formaldehyde in the cold to give the *compound* A, b. p. 108—111°/28 mm.; *picrate*, m. p. 160—161°.

$$(A) \quad CH_2 \Big\langle \begin{matrix} CH_2 \cdot CH_2 \\ CH_2 \text{---} N \end{matrix} \Big\rangle \begin{matrix} CH \cdot CH_2 \cdot CHMe \\ | \\ CH_2 \text{----} O \end{matrix}$$
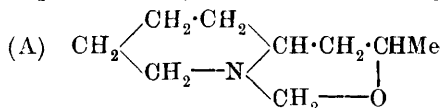
By a mere chance, this compound was obtained earlier by the action of formaldehyde and hydrochloric acid at above 100°. Under these conditions, it has never been obtained since, reaction taking place according to the equation $C_8H_{17}ON + 2H \cdot CHO = C_{10}H_{17}ON + 2H_2O$. The *product* has b. p. 103—107°/23 mm., and forms a *picrate*, m. p. 190°, a *picrolonate*, m. p. 193°, and a *methochloride-aurichloride*, m. p. 98°. It is reconverted into the hydramine by semicarbazide, and is hydrolysed by dilute potassium hydroxide to an *isomeride* of the above compound A; *picrate*, m. p. 192—193°.   J. C. W.

Action of o-Chlorobenzaldehyde on Nitroamines, and a New Scheme for the Preparation of Acridine Derivatives.

Fritz Mayer and Berthold Stein (*Ber.*, 1917, **50**, 1306—1321). —It has been shown that, instead of forming a normal Schiff's base, 1-aminoanthraquinone and o-chlorobenzaldehyde condense together in the presence of a little copper powder and dry sodium carbonate at 220° to yield, among other products, o-1-anthraquinonylamino-

benzaldehyde (A., 1916, i, 843). This abnormal course is ascribed to the repression of the basic functions of the amino-group, owing to the proximity of the carbonyl group, and to the weak attachment of the chlorine atom in the aldehyde. Other feebly basic amines should react, under the same conditions, in the same way, and therefore nitro-amines have been examined in this connexion. Generally speaking, a nitro-group in the ortho-position influences the reaction in the abnormal way, otherwise Schiff's bases are produced. The 2-o-nitroanilinobenzaldehydes can be condensed to nitroacridines by means of concentrated sulphuric acid.

The above principle can be employed in the synthesis of acridine itself. Iodobenzene and o-aminobenzaldehyde are boiled together in nitrobenzene with anhydrous sodium carbonate and some copper powder, the solvent is then removed in a current of steam, the residue is warmed with concentrated sulphuric acid, and finally the solution is diluted and rendered ammoniacal.

The same operations were carried out with o-chlorobenzaldehyde and nitro-bases, as follows.

o-Nitroaniline.—The primary condensation product cannot be crystallised, but the crude material yields 1-*nitroacridine*, in silvery leaflets, m. p. 167°, which induces sneezing, and may be oxidised to the known 1-nitroacridone.

m-Nitroaniline.—This base reacts in the usual way to form a Schiff's compound. As prepared by the above method, 2'-*chloro-3-nitrobenzylideneaniline*, $NO_2 \cdot C_6H_4 \cdot N{:}CH \cdot C_6H_4Cl$, forms grey leaflets, m. p. 116—117°, but if the condensation is carried out under the usual conditions, pale brown needles, with the same m. p., are obtained.

p-Nitroaniline yields 2'-*chloro-4-nitrobenzylideneaniline*, grey leaflets, m. p. 136·5°.

2 : 4-Dinitroaniline.—The primary product is 2-op-*dinitroanilinobenzaldehyde*, $CHO \cdot C_6H_4 \cdot NH \cdot C_6H_3(NO_2)_2$, m. p. 194°, and this is readily converted into 1 : 3-*dinitroacridine*, brown crystals, m. p. 274°.

Under the above conditions, 3-nitro-p-toluidine yields a *double compound* of the Schiff's base and the aldehyde, which forms brownish-yellow crystals, m. p. 127°. If potassium carbonate or sodium acetate is used instead of sodium carbonate, the main product is the Schiff's base, and this is formed when the components are merely warmed together. 2'-*Chloro-3-nitrobenzylidene*-p-*toluidine* has m. p. 145°. On the other hand, if less nitrobenzene and o-chlorobenzaldehyde are used in the condensation, the aldehydo-base is obtained almost pure. Pure 2-m-*nitro*-p-*toluidinobenzaldehyde* is obtained by condensing o-aminobenzaldehyde with 4-chloro-3-nitrotoluene under the above conditions. It crystallises in dark brown leaflets, m. p. 123°, forms an *oxime*, m. p. 160—161°, and may be converted into 1-*nitro-3-methylacridine*, brown needles, m. p. 201—202°, which yields 1-*nitro-3-methylacridone*, glistening, red crystals, m. p. 250°, on oxidation. A mixture of the aldehyde and the Schiff's base in

equimolecular quantities crystallises as the above double compound, m. p. 127°.

4-Nitro-α-naphthylamine yields 2′-*chloro*-4-*nitrobenzylidene*-α-*naphthylamine*, in pale brown scales by the above condensation, or pale yellow needles by the usual method, m. p. 171°.

1-Nitro-β-naphthylamine forms 2′-*chloro*-1-*nitrobenzylidene*-β-*naphthylamine*, in pale brown crystals, m. p. 170—171°.

o-Chlorobenzaldehyde also condenses with 1-amino-2-methyl-anthraquinone under the above conditions, yielding o-2-*methyl-anthraquinonylaminobenzaldehyde*,

$$C_6H_4\!\!<^{CO}_{CO}\!\!>C_6H_2Me\cdot NH\cdot C_6H_4\cdot CHO,$$

in reddish-brown crystals.

o-1-Anthraquinonylaminobenzaldehyde also undergoes internal condensation, but not to the acridine. Apparently, water is not lost, the product being an acridol. This is suggested by the fact that esters can be isolated. Thus, if the aldehydo-amine is heated with a solution of hydrogen chloride in glacial acetic acid at 100°, the *hydrochloride* of *anthraquinonyldihydroacridyl* chloride (annexed formula) may be isolated, in brown crystals, which gradually lose hydrogen chloride on exposure to the air, leaving the free *ester*. A *zincochloride* of the same ester may be obtained, in dark brown leaflets, if zinc chloride is mixed with the acetic acid. Similarly, a *sulphate* of the *sulphuric ester* (same formula) may be isolated. When these salts are mixed with ammonia, it appears that the free dihydroacridol immediately suffers oxidation, the product being anthraquinonylacridone, brownish-red crystals. By a mere chance, a blue compound was once isolated which corresponded better with the acridol.   J. C. W.

Quinolyl Pyrryl Ketones and Quinolylpyrrylcarbinols.

P. KARRER (*Ber.*, 1917, **50**, 1499—1508).—A record of syntheses of compounds showing structural resemblance to quinine, an especial point being that the secondary alcohol group is attached to two cyclic systems, as in quinine.

4-*Quinolyl* 2-*pyrryl ketone*, $N\!\!<^{-C_6H_4-}_{CH\cdot CH}\!\!>C\cdot CO\cdot C\!\!<^{CH-CH}_{NH\cdot CH}$, pale yellow needles, m. p. 153°, prepared by the action of cinchoninoyl chloride hydrochloride in benzene on ethereal magnesium pyrryl iodide, is reduced in aqueous acetic acid by zinc dust and hydrochloric acid, with formation of 4-*quinolyl-2-pyrrylcarbinol*,

$$N\!\!<^{-C_6H_4-}_{CH\cdot CH}\!\!>C\cdot CH(OH)\cdot C\!\!<^{CH-CH}_{NH\cdot CH}$$

colourless crystals, m. p. 177°, which is decomposed by excess of mineral acid, giving a resinous product analogous to pyrrole-red; the parent ketone is soluble without decomposition in dilute hydrochloric acid, giving a yellow solution.

Quinoyl chloride, $\begin{array}{c}\text{CH:C(COCl)}\\ \text{CH}=\!=\!=\!\text{N}\end{array}\!\!> C_6H_4 \cdot OMe$, obtained as the *hydrochloride* in the form of a yellow powder by the action of thionyl chloride on quinic acid, reacts with magnesium pyrryl iodide with formation of 4-(6-*methoxyquinolyl*) 2-*pyrryl ketone,*

$$N <\!\!\begin{array}{c}C_6H_3(OMe)\\ CH \!-\!\!-\!\! CH\end{array}\!\!> C \cdot CO \cdot C <\!\!\begin{array}{c}CH\!-\!CH\\ || \\ NH \cdot CH\end{array},$$
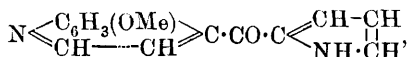
colourless needles, m. p. 153°, which is stable towards excess of mineral acid, giving yellow solutions (*hydrochloride*, colourless; *tribromo*-derivative, $C_{15}H_9O_2N_2Br_3$, yellow needles). The yellow *silver* salt failed to enter into reaction with ethyl iodide, but the expected *N*-ethyl compound is obtainable, although in poor yield, by using magnesium 1-ethylpyrryl iodide in the general synthetic process. Reduction of this ketone is effected in a similar manner to that successful with the quinolyl compound, the resulting 4-(6-*methoxyquinolyl*)-2-*pyrrylcarbinol,*

$$N <\!\!\begin{array}{c}C_6H_3(OMe)\\ CH \!-\!\!-\!\! CH\end{array}\!\!> C \cdot CH(OH) \cdot C <\!\!\begin{array}{c}CH\!-\!CH\\ || \\ NH \cdot CH\end{array},$$
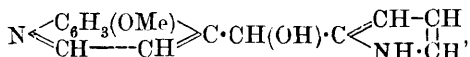
forming a colourless, crystalline powder, m. p. 174°, which dissolves without decomposition in the calculated quantity of hydrochloric acid, but is rapidly converted into a red resin by excess.

6-*Ethoxyquinoline-4-carboxylic acid* is obtained by oxidation of ethyldihydrocupreine, and is further converted into the corresponding *acid chloride hydrochloride,* $\begin{array}{c}\text{CH:C(COCl)}\\ \text{CH}=\!=\!=\!\text{N}\end{array}\!\!> C_6H_3 \cdot OEt, HCl$, by the action of thionyl chloride. The latter product reacts with magnesium pyrryl iodide, yielding 4-(6-*ethoxyquinolyl*) 2-*pyrryl ketone,*

$N <\!\!\begin{array}{c}C_6H_3(OEt)\\ CH \!-\!\!-\!\! CH\end{array}\!\!> C \cdot CO \cdot C <\!\!\begin{array}{c}CH\!-\!CH\\ || \\ NH \cdot CH\end{array}$, colourless needles, m. p. 139°,

which produces yellow solutions in acids, and is reducible by zinc dust and hydrochloric acid in the presence of aqueous acetic acid with formation of 4-(6-*ethoxyquinolyl*)-2-*pyrrylcarbinol,*

$$N <\!\!\begin{array}{c}C_6H_3(OEt)\\ CH \!-\!\! CH\end{array}\!\!> C \cdot CH(OH) \cdot C <\!\!\begin{array}{c}CH\!-\!CH\\ || \\ NH \cdot CH\end{array},$$
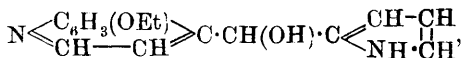
a colourless, crystalline mass, m. p. 185°; this, on treatment with excess of mineral acid, is converted into red, resinous products.

4-(6-*Methoxyquinolyl*) 2-(3:5-*dimethylpyrryl*) *ketone,*

$$N <\!\!\begin{array}{c}C_6H_3(OMe)\\ CH \!-\!\!-\!\! CH\end{array}\!\!> C \cdot CO \cdot C <\!\!\begin{array}{c}CMe \cdot CH\\ || \\ NH \!-\! CMe\end{array},$$
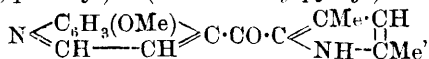
prepared from quinoyl chloride hydrochloride and magnesium 3:5-dimethylpyrryl iodide, is an almost colourless, crystalline mass which gives yellow solutions in mineral acids, and is reducible in

the usual manner to the corresponding 4-(6-*methoxyquinolyl*)-2(3:5-*dimethylpyrryl*)-*carbinol*; this cannot be obtained crystalline, and although it is not reddened by acids, it responds to the pine-shaving test.

The antipyretic action of 4-(6-methoxyquinolyl)-2-pyrrylcarbinol was examined and found to be but slight. It is probable that the corresponding pyrrolidine compound, both chemically and physiologically, would approach more closely to quinine, but the necessary reduction process has not yet been satisfactorily accomplished.

<div align="right">D. F. T.</div>

The Mechanism of the Synthesis of Crystal Violet. P. KARRER (*Ber.*, 1917, **50**, 1497—1499).—It has already been shown that in the coupling of tertiary amines with diazonium salts, attachment of the latter to the former first occurs at the nitrogen atom, after which the azo-radicle migrates to the nucleus. From the observation that Michler's ketone, and also tetraethyldiaminobenzophenone, will undergo condensation with dimethylaniline, diethylaniline, and dipropylaniline, but not with dibutyl- or di*iso*-amyl-aniline, and that condensation in the usual way with the aid of phosphoryl chloride fails with *o*-chlorodimethylaniline and dimethyl-*o*-toluidine, but occurs quantitatively with the corresponding meta-isomerides, the conclusion is drawn that the formation of the final product is preceded by an intermediate coupling at the nitrogen atom, the changes being represented:

$$(NMe_2 \cdot C_6H_4)_2CCl_2 + NMe_2Ph \longrightarrow (NMe_2 \cdot C_6H_4)_2CCl \cdot NClMe_2Ph$$
$$\longrightarrow (NMe_2 \cdot C_6H_4)_2CCl \cdot C_6H_4 \cdot NMe_2 + HCl \longrightarrow$$
$$(NMe_2 \cdot C_6H_4)_2C:C_6H_4:NMe_2Cl.$$
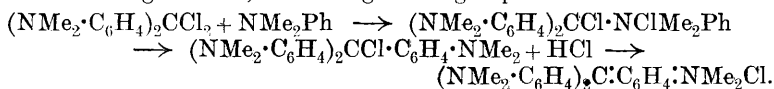
The effect of the butyl and *iso*amyl radicles attached to the nitrogen atom, and of the chlorine atom or methyl group in the ortho-position, is explained by the steric hindrance offered to the primary attachment of the chloro-compound at the nitrogen atom.

<div align="right">D. F. T.</div>

Cyclic Azoxy-compounds. II. FRITZ ARNDT and BRUNO ROSENAU (*Ber.*, 1917, **50**, 1248—1261. Compare A., 1913, i, 1394).—In the earlier paper, it was shown that *o*-nitrophenylguanidine can be prepared by the condensation of *o*-nitroaniline with cyanamide under the influence of concentrated hydrochloric acid. This reaction can be applied to the production of negatively substituted guanidines in general. The following examples are described: m-*nitrophenylguanidine*, yellow leaflets, m. p. 145° (*nitrate*, m. p. 203°); p-*nitrophenylguanidine*, orange-red leaflets, m. p. 188°; *aa-diphenylguanidine*, $NPh_2 \cdot C(NH_2):NH$, m. p. 142° (*nitrate*, long, white needles, m. p. 207°); β-*naphthylguanidine*, m. p. 140° (*nitrate*, m. p. 154°); *benzoylphenylguanidine*,

<div align="center">$NHPh \cdot C(NHBz):NH,$</div>

from aniline and benzoylcyanamide, m. p. 199°; *benzoyl*-m-*nitro phenylguanidine*, pale yellow, velvety needles, m. p. 232°; *benzoyl*-p-*nitrophenylguanidine*, m. p. 219°.

The chief subject of the earlier paper, however, was a reaction which *o*-nitrophenylguanidine and *o*-nitrophenylcarbamide suffer when boiled with dilute alkali hydroxides. Ring closure was shown to occur through the elimination of water, the participating groups being the nitro- and amino-groups. The products are therefore $1:2:4$-benzotriazine-1-oxides. Further examples of this reaction are now given.

One of the new nitro-compounds under investigation is *o*-nitrophenylthiocarbamide, which could not be obtained hitherto. For the preparation of this, *o*-nitroaniline is boiled with thiocarbonyl chloride, when o-*nitrophenylthiocarbimide* is obtained in glistening yellow leaflets, m. p. 73—74°, which reacts with alcoholic ammonia to form the desired product. o-*Nitrophenylthiocarbamide*,

$$NO_2 \cdot C_6H_4 \cdot NH \cdot CS \cdot NH_2,$$
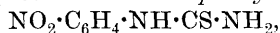
forms yellow crystals, m. p. 136°, which give bright red solutions in alkali hydroxide. When mercuric chloride is added to the alkaline solution, *o*-nitrophenylcyanamide is formed, and this method supersedes the earlier mode of preparation (*ibid.*). If the aqueous alkaline solution is boiled, 3-*thiol*-$1:2:4$-*benztriazine* 1-*oxide*, $C_6H_4 \Big\langle \begin{smallmatrix} NO:N \\ N=C \cdot SH \end{smallmatrix}$, is obtained, in dark red needles, m. p. 184°, which forms a greenish-yellow *methyl ether*, m. p. 123°, and may be oxidised by ammoniacal ferricyanide to the *disulphide*, $C_{14}H_8O_2N_6S_2$, m. p. 205°. (Ring-closure does not follow if the alcoholic alkaline solution is boiled; the product is *o*-nitrophenylcyanamide.) The azoxy-compound may be converted into the pale yellow 3-*thiol*-$1:2:4$-*benztriazine*, m. p. 208—209°, by reduction with zinc dust and dilute sodium hydroxide; the corresponding *methyl ether*, $C_6H_4 \Big\langle \begin{smallmatrix} N:N \\ N:C \cdot SMe \end{smallmatrix}$, yellow needles, m. p. 104°, is obtained by reducing the methylated azoxy-compound.

The above *o*-nitrophenylthiocarbimide was also warmed with aniline and a small quantity of aniline hydrochloride (as a catalyst), when o-*nitrodiphenylthiocarbamide*, $NO_2 \cdot C_6H_4 \cdot NH \cdot CS \cdot NHPh$, was obtained, in yellow crystals, m. p. 142°. If an alcoholic-ammoniacal solution of this is boiled with mercuric oxide, it yields o-*nitro-αβ-diphenylguanidine*, in yellow needles, m. p. 115°, and this may be converted by boiling with sodium hydroxide into 3-*anilino*-$1:2:4$-*benztriazine* 1-*oxide*, $C_6H_4 \Big\langle \begin{smallmatrix} NO:N \\ N=C \cdot NHPh \end{smallmatrix}$: this crystallises in orange-red needles, m. p. 197°, and may be reduced to 3-*anilino*-$1:2:4$-*benztriazine*, orange-red needles, m. p. 197° (mixture melts 20° lower).

The fact that these cyclic azoxy-compounds can be reduced to azo- and hydrazo-compounds (earlier paper and above examples) illustrates their analogy to ordinary azoxy-compounds. This is confirmed by the reverse process, namely, the oxidation of the benztriazines to azoxy-compounds by means of hydrogen peroxide. If Angeli's formula for azoxy-compounds is correct (A., 1913,

i, 658), these cyclic compounds should give two isomeric azoxy-derivatives, the nitrogen atoms of the –N:N– group being differently linked. The products obtained by the action of 33% hydrogen peroxide and glacial acetic acid on 3-amino- and 3-anilino-1:2:4-benztriazine are actually the isomerides of the oxides formed by ring-closure of the nitrated guanidines, which strongly supports Angeli's views. *3-Amino-1:2:4-benztriazine 2-oxide,*

$$C_6H_4 \diagup \substack{N:NO \\ \downarrow \\ N:C\cdot NH_2}$$

yellow needles, m. p. 187°, is much less basic than the 1-oxide, and is decomposed by boiling sodium hydroxide, but both isomerides behave alike on reduction.   *3-Anilino-1:2:4-benztriazine 2-oxide* has m. p. 163°.

The action of nitrous acid on 3-amino-1:2:4-benzotriazine has also been studied. In sulphuric acid solution, the main product is *3-hydroxy-1:2:4-benztriazine,* which crystallises in yellowish-brown needles, m. p. 209—210°, and may be obtained alternatively by reducing 3-hydroxy-1:2:4-benztriazine 1-oxide (*loc. cit.*). The replacement of the amino-group by halogens cannot be effected to any considerable extent through the ordinary diazo-reactions, but with potassium ferro- and ferri-cyanide present, a 10% yield of *3-chloro-1:2:4-*benztriazine may be obtained, in glistening, yellow leaflets, m. p. 100—101°, which irritates the skin, and a similar yield of the *3-bromo-*compound, m. p. 122°.   J. C. W.

The Conversion of Ethyl Acetoacetate into Hydrazidine Derivatives. CARL BÜLOW and RICHARD HUSS (*Ber.,* 1917, **50,** 1478—1496).—An extension of the earlier knowledge that ethyl acetoacetate by conversion into its benzeneazo-derivative and treatment of this with chlorine can be made to yield an oxalic or glyoxylic acid derivative of the structure NHPh·N:CCl·CO₂Et, the chlorine of which is replaceable by the amino- and analogous radicles with formation of hydrazidine compounds of the general formula NHPh·N:C(NHR)·CO₂Et (Bülow and Neber, A., 1913, i, 207, 910, 999; 1916, i, 845).

Ethyl α-methylaminoglyoxylate 2:4-dichlorophenylhydrazone, C₆H₃Cl₂·NH·N:C(NHMe)·CO₂Et, obtained by the interaction of ethyl α-chloroglyoxylate 2:4-dichlorophenylhydrazone and methylamine in alcoholic solution, forms orange-yellow crystals, m. p. 90°, gives a yellow solution in cold sulphuric acid without decomposition, and yields a colourless *hydrochloride.*

Ethyl α-ethylaminoglyoxylate 2 : 4-dichlorophenylhydrazone, C₆H₃Cl₂·NH·N:C(NHEt)·CO₂Et, is obtained by a similar reaction, using ethylamine; the product forms yellow needles, m. p. 95°.

Ethyl α-n-propylaminoglyoxylate 2 : 4-dichlorophenylhydrazone, C₆H₃Cl₂·NH·N:C(NHPrᵃ)·CO₂Et, golden-yellow rhombic crystals, m. p. 102°, prepared in an analogous manner, when treated in

alcoholic solution with chlorine yields a diazo-compound which couples with β-naphthol or R-salt, giving red precipitates, and is probably produced by the reaction

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NHPr^a) \cdot CO_2Et + 2Cl_2 =$$
$$HCl + C_6H_3Cl_2 \cdot N_2Cl + NHPr^a \cdot CCl_2 \cdot CO_2Et ;$$
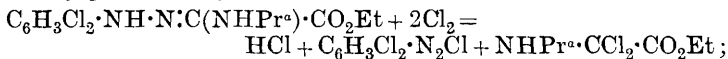
a similar reaction is shown by other members of this group of substances.

Other analogous compounds prepared in a similar manner were *ethyl* α-n-*butylaminoglyoxylate* 2 : 4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_4H_9) \cdot CO_2Et$, yellow needles, m. p. 89°; the isomeric *ethyl* α-iso*butylaminoglyoxylate* 2 :4-*dichlorophenylhydrazone*, canary-yellow needles, m. p. 68·5°; *ethyl* α-iso*amylaminoglyoxylate* 2 : 4-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_5H_{11}) \cdot CO_2Et,$$
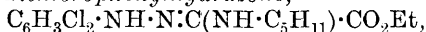
lemon-yellow needles, m. p. 65·5° (*hydrochloride*, colourless; *platinichloride*, yellow needles); *ethyl* α-*benzylaminoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot CH_2Ph) \cdot CO_2Et$, yellow needles, m. p. 89°; *ethyl* α-*anilinoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NHPh) \cdot CO_2Et$, yellow needles, m. p. 90°; *ethyl* α-p-*anisidinoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_6H_4 \cdot OMe) \cdot CO_2Et$, golden-yellow, silky needles, m. p. 158°; *ethyl* α-p-*phenetidinoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_6H_4 \cdot OEt) \cdot CO_2Et$, golden-yellow needles, m. p. 163; *ethyl* α-o-*toluidinoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_6H_4Me) \cdot CO_2Et$, yellow needles, m. p. 130°; *ethyl* α-p-*toluidinoglyoxylate* 2 :4-*dichlorophenylhydrazone*, m. p. 130°; *ethyl* α[α-*naphthylamino*]-*glyoxylate* 2 :4-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_{10}H_7) \cdot CO_2Et,$$
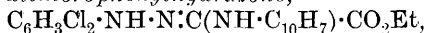
greenish-yellow platelets, m. p. 130°; *ethyl* α[β-*naphthylamino*]-*glyoxylate* 2 :4-*dichlorophenylhydrazone*, orange needles, m. p. 161°; in the case of the preparations involving the use of aromatic amines, it was found necessary to heat the amine with the ethyl α-chloroglyoxylate 2 :4-dichlorophenylhydrazone in the absence of a solvent. *Ethyl* α-*piperidinoglyoxylate* 2 :4-*dichlorophenylhydrazone*,

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NC_5H_{10}) \cdot CO_2Et,$$
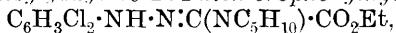
colourless needles, m. p. 124°, and *ethyl* α-*camphylaminoglyoxylate* 2 :4-*dichlorophenylhydrazone*, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_{10}H_{17}) \cdot CO_2Et$, brownish-yellow needles, m. p. 111—111·5°, were also prepared, as also, by the use of α-chloroglyoxylamide 2 :4-dichlorophenylhydrazone in place of the corresponding ester, was α-*piperidinoglyoxylamide* 2 :4-*dichlorophenylhydrazone*.

$$C_6H_3Cl_2 \cdot NH \cdot N{:}C(NC_5H_{10}) \cdot CO \cdot NH .$$
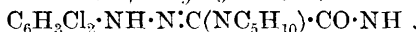
pale yellow needles, m. p. 172°.

Of the "hydrazidine" compounds described above, those derived from aromatic amines are so feebly basic that they dissolve only in strongly acid solutions. All, when dissolved in sulphuric acid, give colorations with oxidising agents such as ferric chloride or

hydrogen peroxide; in dilute solution, sodium nitrite gives a violet-brown coloration or turbidity, the formation of which can be applied as a test for distinguishing between nitrate and nitrite.

D. F. T.

Hydrazides and Azides of Sulphocarboxylic Acids. II. Rearrangement of o-Aminosulphonylbenzoyl Azide.

ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **95**, 392—396. Compare A., 1917, i, 709).—*o*-Aminosulphonylbenzoyl azide does not yield the carbimide, $NH_2 \cdot SO_2 \cdot C_6H_4 \cdot N \colon CO$, when boiled with indifferent solvents, or the corresponding urethane when heated with alcohol, as acid azides usually do, but behaves like 3-nitro-2-carboxybenzoyl azide (A., 1913, i, 472), giving a ring compound. The product, *o-aminosulphonylphenylcarbamic anhydride*,

$$C_6H_4 {<}^{SO_2 \cdot NH}_{NH \cdot CO} \quad \text{or} \quad C_6H_4 {<}^{SO_2 - N}_{NH \cdot C \cdot OH},$$
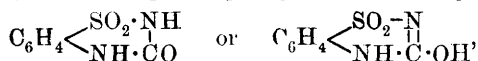
crystallises in slender, glistening needles, m. p. 287—288°, and is converted by prolonged heating with alcohol at 125° into *ethyl o-aminosulphonylphenylcarbamate*, needles, m. p. 137°, and by boiling with aniline into *aniline-o-sulphonamide*,

$$NH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2.$$
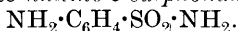
The latter forms stout needles, m. p. 153°, yields a *hydrochloride*, m. p. 201°, and a *benzoyl* derivative, $NH_2 \cdot SO_2 \cdot C_6H_4 \cdot NHBz$, needles, m. p. 198°, and gives a bright red azo-dye with *R*-salt.   J. C. W.

The Special Reactions in the Transformation of the Azides of Carboxylic Acids. XIV.—XVII. Conclusion.

THEODOR CURTIUS (*J. pr. Chem.*, 1917, [ii], **95**, 327—373. Compare A., 1917, i, 635—639).

[With JOHANNES JANSEN.]—XIV. *Hydrazides of Aspartic and* p-*Aminobenzoic Acids.*—*Aspartic monohydrazide* (**α**-amino-β-*carboxypropionhydrazide*), $CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot NH_2, H_2O$, is prepared by the action of hydrazine hydrate on asparagine or ethyl hydrogen aspartate hydrochloride; it crystallises in long needles, m. p. about 174°, is very soluble in water but insoluble in organic media, and is easily hydrolysed. Its ammonium and silver salts are unstable, and the *dihydrochloride* is excessively hygroscopic. It yields a *benzylidene* compound, decomp. 219—225°, a *salicylidene* compound, m. p. 226° (decomp.), and a m-*nitrobenzylidene* compound, m. p. 191°, and also condenses with ethyl acetoacetate to form a *compound*,

$$CO_2H \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot N \colon CMe \cdot CH_2 \cdot CO_2Et,$$
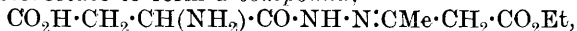
m. p. 168°, which is hydrolysed by water itself.

Aspartic dihydrazide, $N_2H_3 \cdot CO \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot N_2H_3$, is obtained from ethyl aspartate. It is a somewhat hygroscopic, easily hydrolysable solid, m. p. 135° (decomp.), which forms a *trihydrochloride*, a *dibenzylidene* compound, which chars without melting, and a *di*-m-*nitrobenzylidene* compound, m. p. 188°. Anisaldehyde does not give a condensation product, but eliminates hydrazine and forms anisaldazine. When treated with nitrous

acid, the dihydrazide effervesces briskly; the residue, after extracting the product with ether and evaporating the solvent, is changed by boiling with alcohol into a syrup, which reacts with phenyl hydrazine to give glyoxalphenylosazone, the product of the decomposition of the acid azide being, therefore, aminoacetaldehyde.

Ethyl *p*-aminobenzoate, m. p. 92°, b. p. about 310°, reacts with hydrazine hydrate to form p-*aminobenzhydrazide*, which crystallises in long needles, m. p. 220°, and yields a *dihydrochloride*, a *benzylidene* compound, silky needles, m. p. 210°, and a *salicylidene* compound, glistening leaflets, m. p. 220°. A hydrochloric acid solution of the hydrazide reacts with *p*-toluenediazonium sulphate to give p-*aminobenzoyl azide*, $NH_2 \cdot C_6H_4 \cdot CO \cdot N_3$, which separates as a flocculent, crystalline mass. When this is boiled with water or alcohol, it loses one molecular proportion of nitrogen, and the carbimide formed immediately undergoes internal rearrangement into *p*-phenylenecarbamide, $C_6H_4 {<}^{NH}_{NH}{>}CO$.

[With RICHARD COLOSSER.]—XV. *Hydrazides of* α- *and* β-*Dimethylaminopropionic, Dimethylaminosuccinic, and Dimethylanthranilic Acids.*—*Ethyl* α-*dimethylaminopropionate*, a liquid with the odour of turpentine, b. p. 156·5°, is obtained from the bromo-ester and dimethylamine. It reacts with hydrazine hydrate, forming α-*dimethylaminopropionhydrazide*, a soluble syrup, which yields a *dihydrochloride*, m. p. 214°, and a m-*nitrobenzylidene* compound, radiate needles, m. p. 144°, and reacts with nitrous acid to form acetaldehyde, ammonia or dimethylamine, but not hydrazine, as the volatile products.

Methyl β-*dimethylaminopropionate*, from the iodo-ester, yields β-*dimethylaminopropionhydrazide* as a yellow syrup, which forms a *dihydrochloride*, m. p. 146—147° (decomp.), and a *benzylidene* compound, m. p. 131·5°, and does not react with nitrous acid to form the acid azide. On keeping, the hydrazide gradually changes into *bis*-β-*dimethylaminopropionhydrazide*,

$$N_2H_2(CO \cdot CH_2 \cdot CH_2 \cdot NMe_2)_2,$$
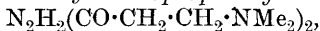
m. p. 115·5°, which forms a *dihydrochloride*, m. p. 126°.

Methyl dimethylaminosuccinate, m. p. 32°, b. p. 115°/18 mm., from the bromo-ester, yields *dimethylaminosuccindihydrazide*, $N_2H_3 \cdot CO \cdot CH_2 \cdot CH(NMe_2) \cdot CO \cdot N_2H_3$, needles, m. p. 147°, which gives a hygroscopic *trihydrochloride*, m. p. 128°, a *dibenzylidene* compound, m. p. 132°, a *disalicylidene* compound, m. p. 216·5°, and a *diisopropylidene* compound, m. p. 137°, and may be converted into glyoxalphenylosazone, like the above aspartic dihydrazide.

Methyl dimethylanthranilate, m. p. 18·5°, yields *dimethylanthranilhydrazide*, $NMe_2 \cdot C_6H_4 \cdot CO \cdot N_2H_3$, m. p. 51°, which forms a *dihydrochloride*, m. p. 165—166°, a *benzylidene* compound, m. p. 115°, a yellow *salicylidene* compound, m. p. 103°, and an iso*propylidene* compound, m. p. 150°. The *azide*, $NMe_2 \cdot C_6H_4 \cdot CO \cdot N_3$, is a very unstable, yellow oil.

[With WALTER DONSELT.]—XVI. *Hydrazides of Tyrosine and*

Benzoyltyrosine.—Tyrosine was obtained by hydrolysing casein, and from *p*-hydroxybenzaldehyde and hippuric acid. The hydrochloride of the ethyl ester may be converted into impure *ethyl α-diazo-β-p-hydroxyphenylpropionate*,   OH·C₆H₄·CH₂·CN₂·CO₂Et, by the method in use for the preparation of ethyl diazoacetate from glycine. *Tyrosine amyl* ester crystallises in pale yellow needles, m. p. 68—70°, and its *hydrochloride* has m. p. 181—182°. Although tyrosine ethyl ester has the same m. p. whether obtained from casein or synthetically, the two specimens give different *hydrazides*, OH·C₆H₄·CH₂·CH(NH₂)·CO·N₂H₃; the "synthetic" hydrazide forms white needles, m. p. 171°, and yields a *dihydrochloride*, decomp. 235·5°, a *dibenzylidene* compound, m. p. 197°, a *disalicylidene* compound, m. p. 205—206°, and a *diisopropylidene* compound, m. p. 149—150°; the "natural" hydrazide has m. p. 195·5°, but yields the same benzylidene compound. With nitrous acid, it gives a crude azide, m. p. 120—140°, but is largely hydrolysed to tyrosine.

Benzoyltyrosine ethyl ester, bundles of needles, m. p. 122—123°, and *amyl* ester, m. p. 106—107° are described. *Benzoyltyrosine hydrazide*, felted needles, m. p. 229—230°, yields a *benzylidene* compound, very slender needles, m. p. 250—251°, a *salicylidene* compound, m. p. 243—244°, and an iso*propylidene* compound, white needles, m. p. 215—216°, and may be converted into the *azide*, OH·C₆H₄·CH₂·CH(NHBz)·CO·N₃, m. p. 72—73° (decomp.). This reacts with ammonia to form *α-benzoylamino-β-p-hydroxyphenylpropionamide*, m. p. 232—233°, identical with a product obtained from the ethyl ester; with aniline, to give the *anilide*, m. p. 212°; and with alcohol, to form the urethane, *ethyl α-benzoylamino-β-p-hydroxyphenylpropylcarbamate*, m. p. 171—172°.

[With NIKOLAOS C. KYRIACOU.]—XVII. *Hydrazide and Azide of Dibenzoyl- and Dihippuryl-cystine.*—A convenient preparation of cystine from human hair is described. Cystine methyl ester dihydrochloride yields an impure *α-bisdiazo*-methyl ester,

$$S_2(CH_2·CN_2·CO_2Me)_2,$$
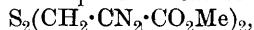
and may be de-aminated to β-dithiodilactic acid,

$$S_2[CH_2·CH(OH)·CO_2H]_2,$$
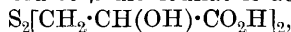
the *calcium* salt of which is a sandy powder.

Dibenzoylcystine methyl ester, m. p. 192—193°, and *ethyl* ester, m. p. 185—186°, form snow-white needles. The *dihydrazide*, $S_2[CH_2·CH(NHBz)·CO·N_2H_3]_2$, is a crystalline mass, m. p. 206—207°, which forms a *dibenzylidene* compound, m. p. 228—230°, and the impure *diazide* is a white mass, which forms a carbamide, m. p. 178° (decomp.), when boiled with water.

Hippuryl azide and cystine react in *N*-sodium hydroxide solution to form *dihippurylcystine*, $S_2[CH_2·CH(CO_2H)·NH·CO·CH_2·NHBz]_2$, which sinters at 65°, intumesces at 120°, and chars at above 160°. The *methyl* ester crystallises in glistening needles, m. p. 113°; the *dihydrazide* decomposes at 160—162°, and forms a *dibenzylidene* compound, m. p. 180° (decomp.), and a *diisopropylidene* compound, m. p. 152—153°; the *diazide* is a very pale pink mass,

m. p. 95—97° (decomp.), which yields the *urethane*,

$$S_2[CH_2 \cdot CH(NH \cdot CO_2Et) \cdot NH \cdot CO \cdot CH_2 \cdot NHBz]_2,$$
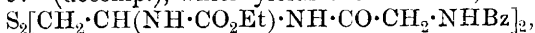
m. p. 168—169°, when boiled with alcohol.

The azides of dibenzoyl- and dihippuryl-cystine change into carbamides when boiled with water. If these are boiled with dilute sulphuric acid, dithiodiacetaldehyde, $S_2(CH_2 \cdot CHO)_2$, distils over with the steam, and the remaining liquid becomes dark blue. The same aldehyde is obtained by hydrolysing *dithiobisdiethyl-acetal*, $S_2[CH_2 \cdot CH(OEt)_2]_2$, b. p. 140—170°/14 mm., which is prepared as an evil-smelling oil by heating bromoacetal with potassium hydrogen sulphide and oxidising the product with iodine. The aldehyde forms a characteristic *di-p-nitrophenylhydrazone*, a yellowish-red powder, m. p. 176—177°.   J. C. W.

Chemical Studies in Physiology and Pathology. I. The Chemistry of the Proteins regarded as the Basis of Vital Processes. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, **83**, 42—61).—A paper of purely theoretical character. The protein is regarded as consisting of an inner core surrounded by layers of adsorbed degradation products of proteins, such as amino-acids and albumoses. It is only when thus surrounded that it exists in a colloidally dispersed condition. Either synthesis or hydrolysis can take place in the adsorbed layer. If hydrolysis takes place, the simpler amino-acids will be formed, and these may pass away; or amino-acids, etc., may be carried to the adsorbed layer, and synthesis take place. The protein molecule thus conceived is supposed to be surrounded by a semipermeable membrane of variable permeability, which regulates the passage of substances to and from the layer of adsorption products. This membrane itself is supposed to be formed from a protein, which, after loosing its adsorbed products, is no longer colloidally dispersed, but becomes insoluble (" denaturated "). The application of this theory to the phenomena of growth, senility, secretion, and immunity is discussed.

S. B. S.

Nuclein Metabolism. IV. The Structure of Yeast-nucleic Acid and its Cleavage by Weak Ammoniacal and Fermentative Hydrolysis. S. J. THANNHAUSER and G. DORF-MÜLLER (*Zeitsch. physiol. Chem.*, 1917, **100**, 121—147. Compare A., 1914, i, 1015).—The triphosphonucleic acid previously obtained by the action of intestinal juice on yeast-nucleic acid has now been prepared by hydrolysis with weak ammonia. After the removal of the ammonia, the hydrolysed yeast-nucleic acid is treated with brucine; three crystalline brucine salts are obtained, which are separated by fractional crystallisation. The least soluble salt is identified as the *brucine* salt of uridine-phosphoric acid, $C_9H_{13}O_9N_2P(C_{23}H_{26}O_4N_2)_2$, m. p. 177°, $[\alpha]_D + 14\cdot4°$; the most soluble brucine salt is that of the triphosphonucleic acid already described, whilst an optically inactive *brucine* salt is also obtained which apparently is that of dl-*triphosphonucleic acid*,

$$C_{29}H_{42}O_{23}N_{13}P_3(C_{23}H_{26}O_4N_2)_6,$$
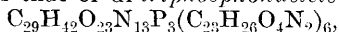
m. p. 185—187°. A repetition of previous work now shows that these three cleavage products are also formed by the action of intestinal juice on yeast-nucleic acid, and are readily separable by the agency of brucine.

The hydrolysis of either of the triphosphonucleic acids by ammonia under pressure yields guanosine, adenosine, and cytidine, whilst the similar hydrolysis of uridine-phosphoric acid liberates the uridine. When yeast-nucleic acid is heated with 2% sulphuric acid at 125°, the triphosphonucleic acids, if formed, are further decomposed, and only the uridine-phosphoric acid appears to be obtainable from the hydrolytic products.

The authors consider that the simultaneous liberation of the trinucleotide, triphosphonucleic acid, and the mononucleotide, uridine-phosphoric acid, indicates that the three constituent mononucleotides in triphosphonucleic acid must be combined in a different manner from the uridine-phosphoric acid in the parent molecule of yeast-nucleic acid. The existence of a hexabrucine salt of triphosphonucleic acid shows that the component mononucleotides must be joined together through the carbohydrate instead of the phosphoric acid radicles (compare Jones and Read, A., 1917, i, 232, 233). They suggest, therefore, that the constituent mononucleotides of yeast-nucleic acid are all joined together through the phosphoric acid groups, whilst the mononucleotides composing the triphosphonucleic acid have additional linkings between the carbohydrate groups. Hydrolysis with dilute ammonia severs only the linking between the phosphoric acid groups, and thus the triphosphonucleic acid and uridine-phosphoric acid are obtained.

The authors are unable to ascertain the relative number of triphosphonucleic and uridine-phosphoric acids present in the parent molecule, but since two of the former have been isolated, they depict the structure of yeast-nucleic acid on the supposition that it contains two triphosphonucleic acid and one uridine-phosphoric acid groups in the molecule.   H. W. B.

The Influence of Formaldehyde on the Digestion of Proteins. FRITZ JOHANESSOHN (*Biochem. Zeitsch.*, 1917, **83**, 28—41).—Finkelberg's pepsin is not injured after remaining for one day in 10% formaldehyde. The various preparations of trypsin, on the other hand, were weakened in their action after remaining with formaldehyde, trypsinogen, after treatment with 0·05%, and Merks's trypsin after treatment with 1% of the aldehyde. Egg-white after remaining for nine days in 1% aldehyde solution is rendered indigestible by pepsin-hydrochloric acid, and its digestibility by trypsin is diminished by about one-fifth. The relationship of the results obtained by the author to those of other investigators is discussed.   S. B. S.

The Theory of Schardinger's Enzyme, and on Reciprocal Influencing of Reducing Agents in some Photochemical Experiments. G. WOKER and H. MAGGI (*Ber.*, 1917, **50**, 1321—1331).—Formaldehyde does not reduce methylene-blue itself

and is able to hinder the reduction of this dye by a number of reductases and also sugars (compare Maggi and Woker, this vol., ii, 22). Schardinger's milk enzyme is peculiar, however, in that formaldehyde does not influence its action on methylene-blue. In the presence of methylene-blue the milk enzyme can also play the part of an oxydase or mutase (compare Wieland, A., 1913, i, 1304). For example, salicylaldehyde is converted into salicyl alcohol and salicylic acid.

These various functions of Schardinger's enzyme are discussed in the light of the author's theory of the aldehydic character of enzymes. As a *reductase*, a "ferment-aldehyde" would react according to the scheme $R_F \cdot CHO + H_2O = R_F \cdot CH(OH)_2 \longrightarrow R_F \cdot CO_2H + 2H$, and, for example, $2H + $ methylene-blue $=$ leuco-base $+ H_2O$. [R $= $ "ferment-radicle."] As an *oxydase* it would act as an acceptor of hydrogen from easily reducible substances, thus: $R_F \cdot CHO + 2H = R_F \cdot CH_2 \cdot OH$; in the presence of oxygen or substances like methylene-blue or quinone which readily give up oxygen, the ferment-aldehyde would be regenerated and then act further on the reducible substance. As a *mutase* it would react, for example, with salicylaldehyde, thus:

(1) $R_F \cdot CH(OH)_2 + CHO \cdot C_6H_4 \cdot OH = R_F \cdot CO_2H + OH \cdot CH_2 \cdot C_6H_4 \cdot OH$.
(2) $R_F \cdot CO_2H + (OH)_2CH \cdot C_6H_4 \cdot OH = R_F \cdot CH(OH)_2 + CO_2H \cdot C_6H_4 \cdot OH$.
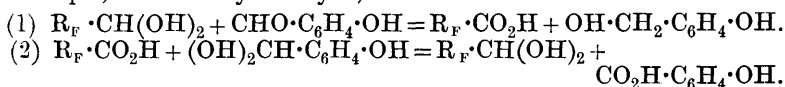
In the presence of substances which readily give up oxygen, more of the ferment-acid, $R_F \cdot CO_2H$, would be formed and, therefore, more salicylic acid.

One aldehyde can act as an acceptor of hydrogen from the hydrate of another aldehyde, and this is what is supposed to happen in the case of formaldehyde and Schardinger's enzyme. The following changes are possible: (a) $R_F \cdot CH(OH)_2 + H \cdot CHO = CH_3 \cdot OH + R_F \cdot CO_2H$; (b) $R_F \cdot CO_2H + H \cdot CH(OH)_2 = H \cdot CO_2H + R_F \cdot CH(OH)_2$. The reduction of methylene-blue by the mixture of formaldehyde and milk may then be due to the direct action of methyl alcohol, thus: dye $+ MeOH =$ leuco-base $+ H \cdot CO_2H$; or indirectly thus: $R_F \cdot CHO + MeOH = R_F \cdot CH_2 \cdot OH + H \cdot CHO$, and $R_F \cdot CH_2 \cdot OH + $ dye $= R_F \cdot CHO + $ leuco-compound. It is possible to test whether the direct reduction can proceed, and it may be shown that methyl alcohol does bleach methylene-blue solutions if exposed to the light. Milk bleaches methylene-blue in the dark, however, but not so well as in the light, so other factors are at work in the action of formaldehyde-milk on the dye.

The reduction of methylene-blue also proceeds quickly in the light, in the presence of nitrites, arsenious oxide, or dextrose, but if these agents are mixed with methyl alcohol, little or no bleaching takes place. This remarkable counteraction between pairs of reducing agents is discussed along somewhat similar lines.   J. C. W.

Physiological Chemistry.

The Sugar of the Blood. S. Gutmann and O. Adler (*Biochem. Zeitsch.*, 1917, **83**, 11—17).—The proteins of the blood were precipitated by Schenk's method, and the reducing action (on copper solutions) of the protein-free blood was determined in the filtrate directly, and after heating with 2·2% hydrochloric acid. No difference was found in the two sets of estimations, whence the conclusion is drawn that the blood contains no polysaccharides. Neither were polysaccharides to be detected when ordinary starch was added to blood, which was then rendered protein-free by Schenk's method. In the case where soluble starch was added, however, the reduction was greater after hydrolysis.   S. B. S.

Residual Reducing Power of the Blood. O. Schumm (*Zeitsch. physiol. Chem.*, 1917, **100**, 215—220).—Polemical against Griesbach and Strassner (see A., 1917, i, 491).   H. W. B.

A New Ferment of the Leucocytes of Blood and Pus : Lipoidase. Noël Fiessinger and René Clogne (*Compt. rend.*, 1917, **165**, 730—732).—The leucocytes of blood and of acute suppuration have the property of secreting an enzyme capable of hydrolysing lecithin in feebly alkaline solution. The enzyme is destroyed by heating at 56—60° in half an hour, and does not act in strongly acid or alkaline solution. The red corpuscles in large quantity and apparently normal serum exert an inhibitory action on the enzyme. This lipoidase is distinguished by its thermolability from the lipase occurring in the leucocytes.   W. G.

The Presence of Phosphates in Human Blood Serum. II. Acid Soluble (Total) Phosphorus, pre-existing Orthophosphoric Acid, and "Residual" Phosphorus in Normal Cases. Joh. Feigl (*Biochem. Zeitsch.*, 1917, **83**, 81—95. Compare A., 1917, i, 520).—The difference between the acid-soluble phosphorus and the orthophosphoric acid which can be estimated directly in the serum is called the residual phosphorus. In the sera of healthy individuals it amounts generally to more than 0·5 mg. per 100 c.c. of serum, or 15% of the total acid-soluble phosphorus. The amount is subject to variations.   S. B. S.

Estimation of Small Amounts of Calcium, particularly in Blood. John O. Halverson and Olaf Bergeim (*J. Biol. Chem.*, 1917, **32**, 159—170. Compare A., 1916, ii, 270).—Full details are given of the method previously described.

Normal serum contains about 10 mg. of calcium in 100 c.c. of serum. The amount of calcium in human milk varies between 27 and 33 mg. per 100 c.c.   H. W. B.

Calcium Content of the Blood-serum in certain Pathological Conditions. JOHN O. HALVERSON, HENRY K. MOHLER, and OLAF BERGEIM (*J. Biol. Chem.*, 1917, **32**, 171—179. Compare preceding abstract).—In nearly all pathological conditions the amount of calcium in the blood-serum does not differ appreciably from that found in health. Slight decreases are observed in some cases of uræmia, eclampsia, and pneumonia. H. W. B.

Diffusion of Electrolytes through the Membranes of Living Cells. V. Additive Effect of Salt and Base and the Antagonistic Effect of Salt and Acid. JACQUES LOEB (*J. Biol. Chem.*, 1917, **32**, 147—158. Compare A., 1917, i, 102).—The author has previously shown that the effects of the addition of a second salt on the diffusion of potassium salts through the membranes of *Fundulus* eggs are analogous to the effects of salts on globulins, which are insoluble in water, soluble in a moderate concentration, and insoluble again in a very high concentration of salt. It is suggested that the diffusion of potassium salts is dependent, therefore, on the solution of a certain constituent of the membrane with properties resembling those of a globulin. This hypothesis is supported by the analogy which is now shown to exist between the effects of salt on the action of acids and bases in the case of the membrane of the *Fundulus* egg and in that of globulins respectively.

When *Fundulus* eggs are put into solutions of bases not sufficiently concentrated to injure the embryo, the bases become injurious when neutral salts in low concentrations are added. An additive effect of salt and base is observed also at higher concentrations of the base. On the other hand, the addition of a neutral salt to an acid which kills rapidly the embryo of *Fundulus* eggs produces an antagonistic effect, which is also observed for lower concentrations of acids. The minimal quantity of a salt required for these effects diminishes with an increase in the valency of both anion and cation of the salt. By comparing the effects on the egg with those on the newly-hatched embryo, it is shown that these additive and antagonistic effects are due, in the case of the egg of *Fundulus*, to an influence of the salt on the rate of diffusion of alkali and acid through the membrane of the egg, accelerating the diffusion of alkali and retarding the diffusion of acid. Since, therefore, salts increase the rate of diffusion of certain electrolytes through the membrane of the egg of *Fundulus* when they are also able to dissolve globulins, and they retard or inhibit the diffusion when they are likely to prevent the solution of globulins, it is probable that the substance in the membrane on which the diffusion of electrolytes depends is a globulin. H. W. B.

Cholesterol in Animal Organs. I. LIFSCHÜTZ (*Biochem. Zeitsch.*, 1917, **83**, 18—27).—Cholesterol was prepared from ox-brain in the usual manner, and sufficient digitonin was added to the alcoholic solution to precipitate about one-third to one-half of

the cholesterol. From this precipitate, the ordinary cholesterol could be isolated by Windaus's method. The filtrate from the digitonin-cholesterol compound yielded, however, a cholesterol which crystallised in an elliptical form and melted after repeated recrystallisations from ethyl and methyl alcohols at 139—141°, or 5° below the m. p. of the ordinary form. From ox-blood, cholesterol was also prepared, and this consisted chiefly of the substance with elliptical form (m. p. 139—141°), from which the acetate (m. p. 109—110°) was prepared. The latter melts about 4° below the acetate of the ordinary cholesterol. The cholesterol of the organs mostly concerned in the resorption of fat consists for the greatest part of ordinary (rhombic) cholesterol, whereas the cholesterol of the kidneys is almost exclusively of the elliptical form.   S. B. S.

Metabolism of Sugar in the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1917, **100**, 185—202).—When the spinal cords of frogs are placed in a saline solution containing dextrose. and oxygen is bubbled through the solution, the dextrose gradually disappears. In the absence of the spinal cords, the dextrose content of the solution remains unchanged. The nerve tissue is therefore capable of inducing glycolysis. The membranes surrounding the spinal cord appear to be impermeable to dextrose, because the glycolysis becomes more pronounced when the membranes are removed before placing in the dextrose-saline solution. In these circumstances, at the ordinary temperature, from 4 to 5 mg. of dextrose per 1 gram of cord disappear in twenty-four hours. The glycolysis varies with the temperature and gradually declines throughout the experiment, being no longer recognisable after the second day. The latter observation indicates that the results cannot be attributed to bacterial action. Lack of oxygen rapidly causes an irreversible decline in the glycolysis; alcohol, ethyl carbamate, and also a trace of a soluble calcium salt (0·1% calcium chloride) lower the glycolysis, but after the removal of the inhibiting agent, it rapidly returns to its former level. Electrical stimulation of the tissue evokes a great acceleration of the rate of disappearance of the dextrose, which reaches twice the normal value.

If the spinal cords are reduced to a fine state of division, the rate of glycolysis is markedly increased, presumably on account of the increased surface of contact between tissue and dextrose solution. It is a function of the living tissue; the boiled material does not induce any glycolysis. The consumption of dextrose by the minced spinal cord is influenced in the same way as in the case of the intact organ by the various factors above described, with the exception that electrical stimulation does not evoke any increase in glycolysis after the normal structure of the tissue has been destroyed.   H. W. B.

The Carbohydrate Metabolism in the Surviving Liver of the Dog. J. ABELIN and J. M^{A.} DE CORRAL (*Biochem. Zeitsch.*, 1917, **83**, 62—73).—Although the perfusion of peptone solution has no influence on the glycogen content of the liver of a rabbit, it diminishes the amount of this carbohydrate in the liver of the dog. Perfusion of adrenaline is without action on the glycogen degradation in the livers both of the rabbit and the dog.

S. B. S.

Biological Analysis of Diets Producing Pellagra. II. Minimum Requirements of the two Unidentified Dietary Factors for Maintenance as contrasted with Growth. E. V. McCOLLUM and N. SIMMONDS (*J. Biol. Chem.*, 1917, **32**, 181—194).—The authors describe feeding experiments on rats in which the relative and absolute quantities of the two factors, "fat-soluble A" and "water-soluble B," in the diet are varied. The former factor is contributed in the form of butter-fat and the latter in wheat-germ, and it is found that 1% of each of these factors in the diet is just sufficient to maintain the weight of adult rats. In these circumstances, however, the life of the animal is uncertain, and the rats may die unexpectedly without any apparently sufficient cause. The life of young rats may be maintained for considerable periods without growth when minimum amounts of the two factors are present, and, subsequently, growth may occur in proportion to the increased amounts of the factors administered. The extent of growth depends on the amount of that factor which is present in relatively the smaller proportion; in other words, increased growth after an increased proportion of "fat-soluble A" does not occur unless the amount of "water-soluble B" is increased to a corresponding extent. The results are illustrated by numerous charts.

H. W. B.

The Significance of the so-called "Steric Hindrance" in Biological Processes. I. The Influence of the Methyl Group in the Ring. OSKAR BAUDISCH and FRANZ KLAUS (*Biochem. Zeitsch.*, 1917, **83**, 6—10).—Attention is directed to the fact that substances containing a methyl group are less reactive biologically than the corresponding substances without this group. The statement is illustrated by reference to the therapeutic action of the rosaniline dyes, of acridine-yellow and trypoflavin, and of atoxyl and its methyl derivatives. In all cases, the more methyl groups a substance contains, the smaller its therapeutic activity. Other instances quoted are the differences between crystal-violet and new-magenta when used as stains by Gram's method, and the differences between chrysarobin and cignolin (non-methylated substance) when employed, according to Unna, for the treatment of psoriasis.

S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. IV. MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **83**, 74—80. Compare A., 1917, i, 528).—In the last communication, it was shown that urease is produced by bacteria which are grown on a medium containing inorganic salts and glycerol, ammonium lactate, sodium aspartate, and leucine, of which the last-named is indispensable. Further investigations have been undertaken to ascertain whether all the above-mentioned organic substances are indispensable for production of the ferment. On leucine alone a certain amount of ferment is produced, but more satisfactory amounts are obtained when the medium contained, in addition to leucine, glycerol and sodium aspartate, or ammonium lactate and sodium aspartate. When sodium lactate alone is employed, even after transference of the bacteria to a medium containing leucine, scarcely any urease is produced. It is to be recalled that bacteria will grow on a medium containing no leucine, but produce no urease. On transference to a medium containing leucine, however, the ferment is formed. In the experiments described in this paper, the bacteria were first grown on media containing various mixtures of the above-named organic substances (sometimes with the addition of leucine), and then, after the second generation of growth, transferred to a medium containing this amino-acid. In the control experiments where this acid was not present, no urease was produced.   S. B. S.

The Extraction of Invertase and Maltase from the Permanent Yeast Preparations made by the Acetone Method. EDUARD BUCHNER and FERDINAND REISCHLE (*Biochem. Zeitsch.*, 1917, **83**, 1—5).—The preparations were washed, and then allowed to act on sugars. No evolution of carbon dioxide took place unless boiled juice were added (to replace the co-enzyme which had been washed out). More carbon dioxide was evolved when dextrose and maltose were added than in the case when the same washed preparation was treated with sucrose, and these experiments indicate that the invertase and maltase can be removed by washing.   S. B. S.

Formation of Hexosephosphate during Alcoholic Fermentation. HANS EULER, OLOF SVANBERG, GRETA HALLBERG, and KARIN BRANDTING (*Zeitsch. physiol. Chem.*, 1917, **100**, 203—208).—On estimating, at intervals of fifteen minutes, the amount of inorganic phosphate present in a fermenting mixture of dextrose, yeast, and disodium hydrogen phosphate, it is found that during the first half of the fermentation the phosphate remains almost unchanged, whilst subsequently rapid combination with dextrose

occurs. The acidity of the mixture remains practically constant throughout the whole period of fermentation. It is suggested that during the first half of the time of reaction a catalyst is formed which accelerates the combination of dextrose and phosphate during the later stages of fermentation.   H. W. B.

Action of Sodium Phosphate on the Lactic Acid Fermentation. Hans Euler and Olof Svanberg (*Zeitsch. physiol. Chem.*, 1917, **100**, 148—158).—The lactic acid fermentation of dextrose by the agency of *Bacterium casei*, E., is accelerated by sodium dihydrogen phosphate and inhibited by trisodium phosphate, but a conversion of the inorganic phosphate into hexosephosphate, such as occurs during the fermentation of dextrose by yeast, cannot be detected. The intermediate formation of lactic acid during the alcoholic fermentation of dextrose occurs, therefore, if it occurs at all, by a process which is probably different from that which is effected by the lactic acid bacilli.   H. W. B.

Amygdalin as Nutriment for Fusarium. H. J. Waterman (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 185—188).— Amygdalin is .assimilated by *Fusarium*, young mycelium being formed, but the addition of emulsin to the amygdalin solution entirely prevents growth. Amygdalin is as satisfactory a nutrient as dextrose in respect to the dry weight of mould obtained.
                    W. G.

The Chemistry of the Higher Fungi. XII. Lenzites sepiaria, Sw., Panus stypticus, Bull., and Exidia auricula Judæ, Fr. Julius Zellner (*Monatsh.*, 1917, **38**, 319—380. Compare A., 1915, i, 1086).—Extraction of *Lenzites sepiaria*, Sw., collected from pine trunks, with light petroleum, yielded a yellowish-brown, fatty oil containing an ergosterol; on extraction with ether, an ergosterol was obtained, together with a yellowish-red resin soluble in aqueous alkali hydroxide. The alcoholic extract was separated into constituents soluble in water, these including mannitol and mycose [trehalose] with small quantities of choline and dextrose, and a fraction insoluble in water containing brown nitrogen-free amorphous substances. The aqueous extract of the fungus contained a carbohydrate which did not reduce Fehling's solution, together with a trace of quinoline and mineral substances. Hydrolysis of the leathery residue insoluble in the above solvents gave rise to dextrose as the main product, together with mannose and glucosamine; indications of pentosans were also observed.
Panus stypticus, Bull., gave similar results, except that two carbohydrates were observed in the aqueous extract, which agreed in properties with Boudier's viscosin and mycetide (these substances have never yet been obtained in a state of purity), and that glucosamine was the only definite substance isolated from the residual insoluble tissue.
With *Exidia auricula Judae*, Fr., similar observations were

made, but no mannose or mycetide was detected in the alcoholic
and aqueous extracts respectively; the viscous constituent in
the aqueous extract on hydrolysis yielded mannose with
a little dextrose, and on oxidation with nitric acid produced only
oxalic acid; it is therefore probable that the mucous substance is
a mannan.   D. F. T.

**The Relationship which Exists, in Plant Tissues, between
the Acid and Basic Elements.** G. ANDRÉ (*Bull. Soc. chim.*,
1917, [iv], **21**, 258—271).—A more detailed account of work already
published (compare A., 1912, ii, 675, 803; 1913, i, 233, 688, 946).
                                                            W. G.

**The Transient Red Colour given by certain Leaves
when Treated with Nitric Acid in the Xanthoproteic Test.**
OTTO GERTZ (*Biochem. Zeitsch.*, 1917, **83**, 129—132).—The author
is in agreement with Lakon (A., 1917, i, 504) that the colour in
question can be due to anthocyanin. In certain plants, however,
the colour is specific for nitric acid, and is not given by other
acids, and in these cases it cannot be due to anthocyanin. The
author ascribes it to a nitroso-derivative of some substance as yet
unidentified. The nitroso-derivative is formed by reduction, and
on further reduction it becomes colourless.   S. B. S.

**A New Plant containing Hydrogen Cyanide, Isopyrum
fumarioides,** L. MARCEL MIRANDE (*Compt. rend.*, 1917, **165**,
717—718).—*Isopyrum fumarioides* contains a cyanogenetic glucoside
and an enzyme capable of hydrolysing it. The plant when in full
flower and nearly in fruit yields 0·249 gram of hydrogen cyanide
from 100 grams of fresh plant material. The green fruits contain
0·115% of hydrogen cyanide. The younger the plant, the greater
is the content of hydrogen cyanide.   W. G.

**Vegetable and Animal Fats and Waxes. I. Fat from
Rice Bran.** ALBERT B. WEINHAGEN (*Zeitsch. physiol. Chem.*, 1917,
100, 159—166).—Rice bran contains 10·94% of fatty substances
soluble in ether. They can be separated into a liquid oil (73%)
and a solid fat (27%). The oil contains 5·3% of phytosterol and
91% of fatty acids, of which 59% is oleic and 31·8% palmitic acid.
The solid portion consists of 4·7% of phytosterol and 90·6% of fatty
acid, which is practically pure palmitic acid. A substance is also
present which can be separated from the phytosterol by fractional
crystallisation from alcohol, in which it is only slightly soluble.
It is found to be a saturated *hydrocarbon*, $C_{27}H_{48}$, m. p. 79·5—80·5.

Rice bran does not contain any glycerol or any phosphorus com-
pounds soluble in ether, and only a trace of alcohol-soluble phos-
pholipoids.   H. W. B.

Organic Chemistry.

Hydrolysis of Organic Haloids and the Corrosion of Metals. HOWARD WATERS DOUGHTY (*J. Amer. Chem. Soc.*, 1917, **39**, 2685—2692).—A qualitative study of the subject. The hydrolysis of carbon tetrachloride by water at ordinary temperatures is negligible, but it is greatly accelerated by the presence of iron or copper, the acceleration being accompanied by corrosion of the metal, which is very well marked with iron, but very slight with copper. This corrosion is very greatly increased by the presence of ammonia, but does not take place in the absence of water or carbon tetrachloride. The products are ferric hydroxide and cupric ammonium chloride.

Certain other organic haloids behave in a manner similar to carbon tetrachloride towards copper, the action being most pronounced with compounds containing a trichloromethyl group. Monohalogen derivatives have practically no action on copper in the presence of water and ammonia, and the presence of two halogen atoms gives no increased effect unless they are attached to the same carbon atom. No effect is observed in the case of halogen substituted in the benzene nucleus.

Tetrachloroethylene may be readily detected in that when allowed to remain in contact with water, ammonia, and copper, the aqueous layer develops a rich red colour.   W. G.

The Relative Stability of Halogen-substituted Aliphatic Acids in Aqueous Solution. W. A. DRUSHEL and G. S. SIMPSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2453—2460).—The authors are engaged on a study of the kinetics of the action of water on halogeno-aliphatic acids, and have so far investigated the sodium salts of the halogeno-acetic acids. Decinormal solutions of the salts were heated in sealed tubes at constant temperatures of 70—90°, and, after different intervals, the free acid and also the sodium haloid were titrated, or, in the case of the trichloroacetate, the sodium hydrogen carbonate formed according to the equation $CCl_3 \cdot CO_2Na + H_2O = CHCl_3 + NaHCO_3$.

With the exception of the case of the trihalogeno-acids, the action of water is a true hydroxylation. It is probable that two reactions take place consecutively in the case of the dihalogeno-compounds, thus, $CHCl_2 \cdot CO_2Na + H_2O = CHO \cdot CO_2H + NaCl + HCl$ and $CHCl_2 \cdot CO_2Na + HCl = CHCl_2 \cdot CO_2H + NaCl$.   As the latter reaction is practically instantaneous, the hydroxylation of the dichloroacetate should appear as a unimolecular reaction, but the observed values do not agree with either a uni- or bi-molecular type. There is found to be more sodium chloride produced than free acid. The

anomaly will be discussed in a later paper (compare also Johanssen, Senter, and others).

The relative stability of these sodium salts in $0.1N$-solutions at 70° is of the order: trichloroacetate, 1; bromoacetate, 1·2; iodoacetate, 3·6; chloroacetate, 26; dichloroacetate, 120. It is remarkable that the iodoacetate is more stable than the bromoacetate, and that the dichloroacetate is so very stable compared with the mono- and tri-chloroacetates.   J. C. W.

a- and β·**Cinenic Acids.** H. RUPE and A. BLECHSCHMIDT (*J. pr. Chem.*, 1917, [ii], **96**, 59—64).—a-Cinenic acid, when heated with dilute sulphuric acid, is converted into an isomeric liquid β-cinenic acid (Rupe and Altenburg, A., 1909, i, 7). The isomeric nature of the two acids is now confirmed by careful analysis of some of the salts of the β-acid (*silver* salt; *magnesium* salt, with $\frac{1}{2}H_2O$; *calcium* salt, with $2H_2O$), the results excluding the possibility of the β-acid being in reality a hydroxy-lactone. The action of hydrogen bromide in acetic acid solution converts both a- and β-cinenic acids into the same bromo-derivative (compare Rupe and Altenburg, *loc. cit.*), the β-isomeride undergoing the change more readily. As the bromo-product on treatment with magnesium carbonate and water yields cinogenic acid, which on distillation gives a-cinenic acid, it is possible to reconvert the β-acid into its a-isomeride. From these results, it appears highly probable that the a- and β-acids are of similar structure.   D. F. T.

The Rôle of Atmospheric Oxygen and Alkali in the Oxidation of Acetone with Potassium Permanganate. Pyruvic Acid as an Intermediate Product. EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1917, **39**, 2657—2671. Compare A., 1916, i, 372).—A study of the oxidation of acetone by potassium permanganate in the presence of varying amounts of potassium hydroxide. In the absence of alkali, acetone is not perceptibly oxidised by potassium permanganate at the ordinary temperature. In the presence of small amounts of alkali, the oxidation is incomplete, but in the presence of sufficient alkali the acetone is oxidised solely to acetic and oxalic acids and carbon dioxide in such a way that one molecule of carbon dioxide is formed for each molecule of acetic and oxalic acids, thus:

$$COMe_2 + 4O = CH_3 \cdot CO_2H + CO_2 + H_2O.$$
$$COMe_2 + 7O = C_2O_4H_2 + CO_2 + 2H_2O.$$
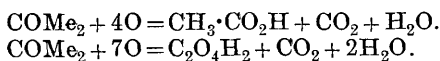
The proportion of oxalic acid increases gradually but continually with increasing alkalinity, indicating that the formation of oxalic acid is dependent on a molecular transformation that is catalysed by or dependent on the alkali. On the basis of Denis's work (compare A., 1907, i, 997) and the intermediate formation of pyruvic acid as shown by Fournier (compare A., 1908, i, 247), the author

gives the following series of changes for the oxidation of acetone by potassium permanganate in the presence of alkali,

$$COMe_2 \longrightarrow CH_2\!:\!CMe\cdot OH \longrightarrow HO\cdot CH_2\cdot CMe(OH)_2 \longrightarrow$$
$$CHO\cdot CMe(OH)_2 \longrightarrow CO_2H\cdot CMe(OH)_2 \longrightarrow$$
$$\longrightarrow CH_3\cdot CO_2H + CO_2$$

$$CH_3\cdot CO\cdot CO_2H$$
$$\longrightarrow CH_2\!:\!C(OH)\cdot CO_2H \longrightarrow C_2O_4H_2 + CO_2.$$
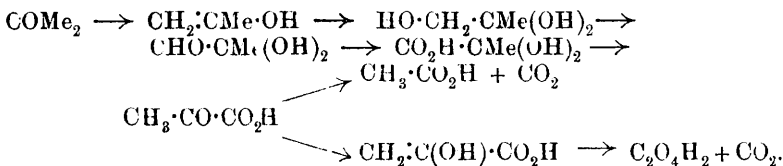
comparable with the formation of iodoform, as explained by Pieroni and Tonnioli (compare A., 1914, i, 6). The functions of the alkali in the oxidation are: (1) to give rise to the active enol, *isoacetone*; (2) to cause the enolisation of pyruvic acid; (3) to neutralise the acids formed, and thus prevent their further oxidation; (4) to determine the velocity of oxidation; and (5) to catalyse the absorption of atmospheric oxygen. W. G.

The Distillation of Cellulose and Starch in a Vacuum. AMÉ PICTET and J. SARASIN (*Compt. rend.*, 1918, **166**, 38—39).— When cellulose or starch is heated gradually under a pressure of 12—15 mm., the fraction distilling between 200° and 300° amounts to about 45 per cent. of the original, and consists of an oily, crystalline paste, from which crystals have been separated corresponding in properties with Tanret's *laevoglucosan*, $C_6H_{10}O_5$ (A., 1894, i, 564) (see, further, *J. Soc. Chem. Ind.*, 1918, **37**, Feb.).

J. F. B.

Pine-wood Lignin. PETER KLASON (*Svensk. kem. Tidskrift,* 1917, **29**, 5—16, 47—52; from *Chem. Abstr.*, 1917, **11**, 2482—2483).—The lignin was obtained from sulphite waste by two procedures: (*a*) by saturating the waste liquors with calcium chloride, and (*b*) by adding to the filtered liquor naphthylamine hydrochloride. The sample (*a*) was purified as the barium salt and (*b*) as the calcium salt. These salts were analysed. The first lignin had a composition suggesting that it was composed of 1 mol. of coniferyl alcohol and 3 mols. of hydroxyconiferyl alcohol, $C_{40}H_{48}O_{15}$ (MeO, 11·55% found; 12·4% calc.). The second lignin (*b*) corresponds with 4 mols. of hydroxyconiferyl alcohol and 6 mols. of trihydroxycinnamyl alcohol, $C_{94}H_{108}O_{40}$. Klason's conception of lignins is that they are formed by condensation of phenols with side-chains in positions 1, 3, 4, in a manner not unlike the proteins and dextrins. The sulphite process breaks up the larger molecules. Molecular weight determinations correspond with formulæ twice the size of the above. Coniferyl alcohol is always the chief component of native lignin, and this explains the formation of

$$C_6H_3Me(OMe)\cdot OH,$$
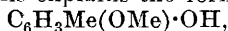
$C_6H_3(C_3H_5)(OMe)\cdot OH$, and $C_6H_3(C_3H_7)(OMe)\cdot OH$ on destructive distillation of wood. Pure lignin and coniferyl alcohol both give several colour tests, but the latter only on keeping. Freshly prepared from an emulsion extracted with ether, it does not react.

G. B.

e 2

Identity of Cyanuric Acid with so-called Tetracarbimide.
E. H. WALTERS and LOUIS E. WISE (*J. Amer. Chem. Soc.*, 1917,
39, 2472—2477).—Scholtz described a product obtained by the
oxidation of uric acid by hydrogen peroxide in alkaline solutions
as "tetracarbimide" (A., 1902, i, 140), and this has not been
called into question until recently, when Venable and Moore sug-
gested that the compound was really cyanuric acid (*J. Amer. Chem.
Soc.*, 1917, **39**, 1750). The identity of the substance with cyanuric
acid is now fully established, optically, titrimetrically (thymol-
phthalein as indicator), and by the characteristic copper salt.

In an application of Scholtz's method with slight modifications,
a small amount of carbonyldicarbamide has been obtained from
uric acid. It might be that this is an intermediate product
between uric and cyanuric acids, for it readily loses ammonia, and
so produces the latter acid.

Cyanuric acid has now been isolated from some eighteen different
soils (compare A., 1917, i, 622). J. C. W.

**Conversion of Methyleneaminoacetonitrile into Imino-
diacetonitrile.** J. R. BAILEY and H. L. LOCHTE (*J. Amer.
Chem. Soc.*, 1917, **39**, 2443—2444).—Bailey and Snyder have re-
ported that methyleneaminoacetonitrile unites directly with
hydrogen cyanide to form iminodiacetonitrile, $NH(CH_2 \cdot CN)_2$
(A., 1915, i, 389). Delépine had previously stated that these com-
pounds do not react together at all (*Bull. Soc. chim.*, 1903, [iii],
29, 1202), and the present authors have now found that a catalyst
is necessary. Pure hydrogen cyanide does not combine with
methyleneaminoacetonitrile, but if a trace of hydrochloric acid is
added to the mixture, the reaction proceeds quickly to completion.
The original agent contained hydrochloric acid as a preservative.
J. C. W.

Hydrolysis of Sodium Cyanide. FREDERICK PALLISER
WORLEY and VERE ROCHELLE BROWNE (T., 1917, **111**, 1057—1062).
—The degree of hydrolysis is measured by passing a current of
air through the sodium cyanide solution and absorbing the
hydrogen cyanide from the issuing gas by means of a solution con-
taining 0·2% of picric acid and 2% of sodium carbonate. This
indicator solution is changed to a reddish-brown colour, which is
matched against the colours produced when the same current of
air is made to pass through aqueous solutions of hydrocyanic acid
containing respectively slightly more and slightly less free acid
than the solution of sodium cyanide under investigation. The
strengths of the hydrocyanic acid solutions required are determined
by preliminary tests. In the actual determination, the three
flasks, to each of which is attached an absorption tube containing
the same volume of indicator solution, are arranged in series, the
sodium cyanide solution being in the middle.

The results obtained are in very satisfactory agreement with
the mass law expressed by the equation $P^2 C/100(100-P)=k$, in

which C is the molar concentration of the cyanide and P the percentage hydrolysis. The value of C was varied from 0·0073 to 5·2 mols. per litre. The influence of temperature on the hydrolysis is shown by the fact that $k \times 10^4$ increases from 0·135 at 0° to 0·484 at 25° and 0·72 at 30°.   H. M. D.

The Action of Aluminium Chloride on Cymene. A. W. SCHORGER (*J. Amer. Chem. Soc.*, 1917, **39**, 2671—2679. Compare Boedtker and Halse, A., 1917, i, 124).—When cymene is heated with aluminium chloride at from 60—150°, the products are $\beta\gamma$-dimethylbutane, benzene, toluene, *m*-xylene, and 1-methyl-3:5-di*iso*propylbenzene. Small amounts of the catalyst favour the formation of toluene, whilst the formation of benzene increases with the amount of catalyst used.

1-*Methyl*-3:5-*diisopropylbenzene*, as isolated, has b. p. 215—218°, D^{20} 0·8668, n_D^{20} 1·4950, and on oxidation with nitric acid (D 1·15) yields uvitic (*s*-methyl*iso*phthalic) acid, giving a *dimethyl* ester, m. p. 98°. With chlorosulphonic acid, the hydrocarbon gave a thiochloride, which with ammonia yielded a *thioamide*, m. p. 92°.
                    W. G.

Action of Benzenesulphonyl Chloride on Organic Bases in Anhydrous Ether. GEORGE L. SCHWARTZ AND WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 2444—2453).—In continuation of Dehn's studies on the production of additive compounds of bases and haloids, especially acid chlorides, in anhydrous ether (A., 1912, i, 833; 1914, i, 1169; 1915, i, 954, etc.), the behaviour of benzenesulphonyl chloride has been investigated. As before, the reagents have been mixed in a large excess of ether, and any precipitates formed, immediately or after days or even months, have been analysed.

In harmony with previous results, it is found that (1) the initial reaction is additive, (2) the reactions are non-ionic, (3) and that light promotes reaction.

With primary and secondary amines, the additive product soon gives place to a greater or less extent to the hydrochloride of the base, thus, $C_6H_5 \cdot SO_2Cl + RNH_2 = SO_2Ph \cdot RNH,HCl$, and this $= SO_2Ph \cdot RNH + HCl \longrightarrow RNH_2,HCl$. The benzenesulphonyl derivative of the base remains in solution. The secondary reactions are promoted by heat, traces of water, and by the free bases. Thus aniline, the toluidines, propylamine, hexylamine, benzidine, phenylhydrazine, carbamide, diethylamine, dipropylamine, di*iso*butylamine, di*iso*amylamine, methylaniline, ethylaniline, piperidine, and dibenzylamine give mixtures of the additive compound and the hydrochloride of the base. The appearance and analysis of the precipitates and the speed of the reactions are recorded. Phenylhydrazine and carbamide give precipitates which contain as much as 82% and 94% of the additive compounds respectively, but the other bases fall very short of this.

With tertiary bases, additive compounds of the types $B,C_6H_5 \cdot SO_2Cl$ and $B_2,C_6H_5 \cdot SO_2Cl$ are formed, but these may be contaminated by other salts if traces of moisture are not excluded, thus, $C_6H_5 \cdot SO_2Cl,B + H_2O \longrightarrow C_6H_5 \cdot SO_3H + B,HCl$, and, subsequently, $C_6H_5 \cdot SO_3H,B$. Tribenzylamine gives a *compound*, B_2X, microscopic prisms, m. p. 174—176°; tripropylamine yields a *compound*, BX, long needles, m. p. 52°; pyridine forms *compounds*, BX, microscopic prisms, m. p. 110—112°, and B_2X, large, rectangular plates; α-picoline gives a *compound*, B_2X; quinoline forms *compounds*, BX, needles, and B_2X, stout rhombs; quinaldine gives a mixture of mono- and di-derivatives; acridine gives a *compound*, B_2X, golden, prismatic needles, m. p. 192°; antipyrine forms a *compound*, BX, needles.   J. C. W.

Dichloroamine T and Chlorinated Eucalyptol (D 1·2).

ROBERT B. KRAUSS and EDWARD CREDE (*J. Amer. Chem. Soc.*, 1917, **39**, 2720—2722).—An improved method is given for the preparation of dichloroamine T [toluene-*p*-sulphodichloroamide] on a large scale, by which a stable product is obtained. When chlorine is passed into eucalyptol in good daylight at such a rate that the temperature does not exceed 80°, chlorinated oil (D 1·2) is obtained which can be used as a solvent for dichloroamine T for surgical purposes without requiring the addition of prepared paraffin oil as a diluent. By further chlorination of the oil (D 1·2), either directly at 100° or in boiling chloroform solution, an amber-coloured oil (D 1·4) is obtained of the consistency of molasses.
                                                                          W. G.

Solubilities of Anthracene, Anthraquinone, *p*-Dibromobenzene, Phenanthrene, and Iodine in Various Solvents.

JOEL H. HILDEBRAND, E. T. ELLEFSON, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1917, **39**, 2301—2302. Compare this vol., ii, 36).—The solubility of anthracene, anthraquinone, *p*-dibromobenzene, phenanthrene, and iodine has been determined at 25° in the solvents alcohol, benzene, carbon disulphide, carbon tetrachloride, ethyl ether, and hexane. In all cases except that of iodine, the amount dissolved was determined by evaporation of the solvent from a weighed portion of the saturated solution; in the case of iodine, the estimation was effected by titration with sodium thiosulphate solution. The following values, in grams of solute per 100 grams of solvent, were obtained: Alcohol solution: 0·328 anthracene, 0·437 anthraquinone, 10·35 *p*-dibromobenzene, 4·91 phenanthrene. Benzene solution: 1·86 anthracene, 83·8 *p*-dibromobenzene, 59·5 phenanthrene. Carbon disulphide solution: 2·58 anthracene, 90·0 *p*-dibromobenzene, 80·3 phenanthrene. Carbon tetrachloride solution: 0·732 anthracene, 36·6 *p*-dibromobenzene, 26·3 phenanthrene. Ethyl ether solution: 1·42 anthracene, 0·104 anthraquinone, 71·3 *p*-dibromobenzene, 42·9 phenanthrene. Hexane solution: 0·37 anthracene, 25·9 *p*-dibromobenzene, 9·15 phenanthrene, and 1·32 iodine.   J. F. S.

Miscibility in the System Aniline-Water-Glycerol.
I. M. KOLTHOFF (*Chem. Weekblad*, 1917, **14**, 1081—1089).—At
18°, glycerol of 89% strength is miscible with aniline in all pro-
portions, a fact which affords a basis for a method of estimating
the proportion of water in glycerol.   A. J. W.

Acid and Basic Properties of Various Compounds.
H. I. WATERMAN (*Chem. Weekblad*, 1917, **14**, 1126—1131).—An
investigation of the alkali and acid equivalents of various sub-
stances, determined by the effect produced on the decomposition of
monoses by sodium hydroxide, and the inversion of sucrose by
hydrochloric acid. Sulphanilic acid has no basic character, and
salicylic acid differs from its isomerides by displaying the proper-
ties of a monobasic acid. Structural formulæ to acount for these
phenomena are suggested.   A. J. W.

**A Catalytic Decomposition of certain Phenol Silver
Salts. II. Thermal Decompositions: The Formula of
the Unpolymerised Residues.** W. H. HUNTER and F. E.
JOYCE (*J. Amer. Chem. Soc.*, 1917, **39**, 2640—2646. Compare A.,
1916, i, 717).—When p-chlorophenol is brominated in glacial acetic
acid solution, it yields 4-*chloro*-2 : 6-*dibromophenol*, needles, m. p.
92°, giving a *silver* salt, occurring in an orange and a white form.
When this silver salt is boiled in benzene, it yields a white,
amorphous solid which is a mixture of the two *compounds*
$(C_6H_2OClBr)_n$ and $(C_6H_2OBr_2)_n$ in the proportion of 1 : 0·86.
When the silver salt is treated with ethyl iodide in the cold, it
gives these two compounds, together with some 4-*chloro*-2 : 6-*di-
bromophenetole*, m. p. 52·5°.

If p-chlorophenol is dissolved in an excess of aqueous potassium
hydroxide, and to the solution is added a solution of potassium
iodate and another of iodine in potassium hydroxide, on gradually
acidifying this mixture, with continual shaking, 4-*chloro*-2 : 6-*di-
iodophenol*, m. p. 107—108°, is obtained, giving a pale yellow
silver salt. When boiled in benzene, the silver salt gives a mix-
ture of the two *compounds* $(C_6H_2OClI)_n$ and $(C_6H_2OI_2)_n$ in the
proportion of 1 : 0·61.

The *silver* salt of 2 : 6-dichloro-4-bromophenol is also decomposed
by hot benzene, giving the two compounds $(C_6H_2OClBr)_n$ and
$(C_6H_2OCl_2)_n$ in the proportion of 1 : 2·26.

In each of these cases it was found that the molecules of the
silver salt split up, losing some of their halogen from the ortho-
position and some from the para-position, the ratio varying widely
between the different salts. There are slight indications that the
halogen in the para-position is the more readily removed, and that
the ease of removal of the halogens is in the descending order,
iodine, bromine, chlorine.

By the decomposition of the silver salt of 4-chloro-2 : 6-dibromo-
phenol by ethyl iodide, more of the molecules lost their halogen
from the ortho-position than in the decomposition by hot benzene.
                    W. G.

Basic Salts of the Metals of the Alkaline Earths. F. BELLONI and E. BACCI (*Gazzetta*, 1917, **47**, ii, 159—170).—The *compound*, $Ba_2(SO_3 \cdot C_6H_4 \cdot OH)_3 \cdot OH,8H_2O$, is obtained in prismatic crystals when a warm dilute solution of phenolsulphonic acid is neutralised with barium hydroxide until it becomes alkaline to phenolphthalein. Of the eight molecules of water contained in this salt, four are lost when it is kept over sulphuric acid, three more at 130°, and the other only after prolonged heating at 170°. When a dilute solution of the salt is treated with carbon dioxide, barium carbonate is precipitated, and barium phenolsulphonate can be recovered from the solution.

The *compound*, $Ba_2(SO_3 \cdot C_6H_4 \cdot OH)_2(OH)_2,4H_2O$, is produced by boiling a solution of 20 grams of barium phenolsulphonate in 200 c.c. of water with 15 grams of barium hydroxide. It is a white powder, very slightly soluble in water. When this solution is treated with carbon dioxide, barium carbonate is precipitated, but the filtrate on concentration yields the monobasic phenolsulphonate first described.

The *compound*, $Ca_2(SO_3 \cdot C_6H_4 \cdot OH)_2(OH)_2,4H_2O$, is prepared by boiling a solution of phenolsulphonic acid with an excess of lime.

The *compound*, $Ba_3(CO_2 \cdot C_6H_4 \cdot OH)_2(OH)_4(OH_2)_2,4H_2O$, is obtained by pouring a solution of sodium salicylate (6 grams) and sodium hydroxide (1 gram) in 50 c.c. of water into a boiling solution of 6 grams of barium chloride in 50 c.c. of water.

The constitution of these and other basic salts of the metals of the alkaline earths is discussed, and formulæ are assigned to them derived from the theories of Werner.   R. V. S.

The Substitution Products of the Aminophenols and of their Derivatives. WALTER FUCHS (*Monatsh.*, 1917, **38**, 331— 341).—The knowledge of the relative effect of the amino- and hydroxyl radicles in the aminophenols in directing the position of entry of a new substituent into the nucleus is not complete, and the behaviour of *p*-aminophenol and its ortho-isomeride towards bromination has been examined. By the careful addition of a chloroform solution of bromine to *p*-aminophenol dissolved in a mixture of chloroform and ether, a green reaction product was obtained which, from the fact that on treatment with ethyl sulphate and alkali it yielded a quantity of 3 : 5-dibromo-4-aminophenetole, must have contained 3 : 5-dibromo-4-aminophenol ; the two bromine atoms had therefore been directed into the two ortho-positions to the amino-group. *p*-Acetylaminophenol when treated with bromine in a similar manner gave rise to 2 : 6-dibromo-4-acetylaminophenol, the influence of the hydroxyl group predominating over that of the acetylamino-radicle ; this product on ethylation gave 2 : 6-*dibromo*-4-*acetylamino-phenetidine*, $NHAc \cdot C_6H_2Br_2 \cdot OEt$, needles, m. p. 198°. Attempts to brominate *o*-aminophenol proved less satisfactory, but it is possible that some 3 : 5-dibromo-2-aminophenol was formed. As a result of this and earlier investigations (Fuchs, A., 1915, i, 520 ;

Reverdin and Düring, A., 1899, i, 266; Hodurek, A., 1897, i, 276; Möhlau and Ohmichen, A., 1882, 395), the scheme

$$NH_2 > (OH, OAlk) > NHAc$$
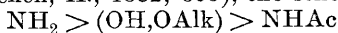
may be given to represent the relative directing power of the groups towards a new substituent, the positions of the hydroxyl and alkyloxy-groups relative to one another remaining yet to be decided. D. F. T.

Molecular Rearrangements in the Camphor Series. XIII. The Decomposition Products of the Methyl Ester of *iso*Aminocamphonanic Acid. A New Reaction Involving the Formation of the Methyl Ether of a Hydroxyacid. WILLIAM A. NOYES and GLENN S. SKINNER (*J. Amer. Chem. Soc.*, 1917, **39**, 2692—2718).—It has been shown in an earlier paper (A., 1913, i, 161) that *iso*aminocamphonanic acid is decomposed by nitrous acid, with the formation of *cis*-camphonolactone, an unsaturated acid, b. p. 150°/60 mm. (decomp.), and a saturated acid, which decomposes at 160°. The present work was undertaken with the object of studying the behaviour of the methyl ester of this acid towards nitrous acid.

A much better yield of $\alpha\beta$-methyl *l-iso*camphorate was obtained by doubling the amount of sulphuric acid previously used (*loc. cit.*) and reducing the time of heating to five hours. The following physical properties of the ester are given: b. p. 130°/8 mm., 138°/13 mm., 141·5°/16 mm., 144°/19 mm., 146°/22 mm.; $[\alpha]_{P}^{24\cdot5} - 65\cdot5°$ and $[\alpha]_{D}^{22} - 66\cdot5°$ in 10·7% alcoholic solution.

β-Methyl α-*l-iso*camphoramate has m. p. 127—128° (corr.) and $[\alpha]_{D}^{28} - 55\cdot4°$ in 10% absolute alcoholic solution (compare *loc. cit.*). From this ester a much better yield of methyl *iso*aminocamphonanate by the method previously described is obtained if the heating is reduced to five minutes. The ester has b. p. 135—138°/10—12 mm.; $[\alpha]_{D}^{26} - 49°$ and $[\alpha]_{D}^{25} - 41\cdot2°$ in 10·5% alcoholic solution. Its hydrochloride has m. p. 179—180° (corr.).

This hydrochloride when decomposed by nitrous acid yields at least six products, namely, the methyl ether and the methyl ester of *cis*-camphonolic acid, and the methyl esters of lauronolic acid, 1 : 2 : 2-trimethyl-Δ^4-*cyclo*pentene-1-carboxylic acid, *cis*-2-hydroxy-1 : 2 : 3-trimethyl*cyclo*pentane-1-carboxylic acid, and a secondary β-hydroxy-acid.

The *methyl ether* of cis-*camphonolic acid* has m. p. 87° (corr.), $[\alpha]_{D}^{28} + 72\cdot1°$, gives *cis*-camphonolactone by treatment with hydrogen iodide, and can be synthesised by the action of methyl iodide on the silver salt of *cis*-camphonolic acid. It gives a *silver* salt and a *methyl* ester, m. p. 116—118°/28—29 mm., $[\alpha]_{D}^{22} + 64\cdot7°$ in 9% alcoholic solution.

1 : 2 : 2-*Trimethyl-*Δ^4*-cyclopentene-1-carboxylic acid* has b. p. 135°/14 mm.; D_4^{20} 1·0132; D_4^{24} 1·0088; $[\alpha]_{D}^{25} + 105\cdot2$ and in 10% alcoholic solution $[\alpha]_{D} + 83\cdot4°$; n_{D}^{25} 1·47256; n_{D}^{25} 1·47560; n_{F}^{25} 1·48279; n_{G}^{25} 1·48887. The *methyl* ester has b. p. 75°/9 mm., 78·5°/15 mm.; $[\alpha]_{D}^{26\cdot5} + 76\cdot6°$. In 10% alcoholic solution it has $[\alpha]_{D}^{24} + 74\cdot4°$; n_{C}^{25} 1·45454; n_{D}^{25} 1·45755;

*e**

n_F^{25} 1·46423 ; $n_{G'}^{25}$ 1·4697.   The structure of this acid was proved by its oxidation to an inactive tribasic acid, which decomposed at its melting point, giving off carbon dioxide.

cis-2-*Hydroxy*-1 : 2 : 3-*trimethyl*cyclo*pentane*-1-*carboxylic acid* has m. p. 101—102°, $[\alpha]_D^{26} + 35\cdot6°$ in 7% alcoholic solution.   It gives *sodium, calcium,* and *silver* salts.   It is not oxidised by Beckmann's chromic acid mixture in the cold, and does not give a lactone by this treatment.   It gives a comparatively stable, crystalline *iodide,* m. p. 85—87°, which when treated at once with sodium hydroxide yields lauronolic acid and no lactone.   The *methyl* ester has b. p. 112—114°/18 mm.

The decomposition of the esters of aminocamphonanic and amino-dihydrocampholytic acids by nitrous acid was also examined, but in neither case was an ether acid obtained.   Methyl *d*-camphorate, b. p. 155°/25 mm., or 144°/15 mm., $[\alpha]_D^{19} + 47\cdot5°$, gives β-methyl α-*d*-camphoramate, m. p. 154—155°, $[\alpha]_D^{24} + 23\cdot1°$ in 9·7% alcoholic solution, which yields methyl aminocamphonanate hydrochloride, m. p. 237°, $[\alpha]_D^{30} + 26\cdot2°$ in 10·7% alcoholic solution.   This hydro-chloride is decomposed by hydrochloric acid, giving a *methyl* ester, b. p. 78—85°/15 mm., $[\alpha]_D^{25\cdot5} + 73\cdot8°$ in 9·25% alcoholic solution, of an unsaturated *acid,* b. p. 125—130°/10 mm., $[\alpha]_D^{28\cdot5} + 108\cdot1°$; D_4^{20} 1·0130.   W. G.

Pyro-condensations in the Aromatic Series.   III.   HANS MEYER and ALICE HOFMANN (*Monatsh.,* 1917, **38**, 343—358.   Compare A., 1917, i, 641).—Azobenzene vapour when heated strongly is liable to decompose suddenly.   *p*-Toluidine when heated, readily underwent decomposition with formation of *pp'*-diaminodibenzyl and a little resinous matter, whereas *o*-toluidine was surprisingly resistant, yielding only a small quantity of anthracene and of un-crystallisable resins ; benzonitrile also proved remarkably stable, and remained unaltered unless the temperature was raised so high as to cause complete decomposition.   Phthalimide at 480° under-went rapid and almost quantitative conversion into benzonitrile, *iso*phthalimide probably occurring as an intermediate product. The presence of chlorine increases the stability of the phthalimide molecule, and whereas the decomposition of phthalimide was already appreciable at 350°, 4-chlorophthalimide formed *p*-chlorobenzo-nitrile only very slowly at 500°, whilst tetrachlorophthalimide, even at its temperature of carbonisation, in the neighbourhood of 600°, gave only sufficient nitrile to be detected by the odour.

The gradual thermal decomposition of benzoic acid gave rise to benzene, benzaldehyde, diphenyl, diphenyl-4-carboxylic acid, and a small quantity of diphenyl-4 : 4′-dicarboxylic acid ; the formation of benzaldehyde is probably due to the reduction of benzoic acid by hydrogen already formed in the decomposition of part of the acid. Ethyl benzoate at a dull red heat was rapidly converted into the free acid and ethylene, but the methyl ester was much more stable and required a still higher temperature for its decomposition, then yielding benzene, diphenyl, methyl diphenyl-3-carboxylate and

diphenyl-4-carboxylate, and trioxymethylene; in a similar manner, the methyl group in toluene was retained by the benzene nucleus, and in ethylbenzene only the end carbon atom of the ethyl group suffered scission, the carbon atom adjacent to the benzene ring remaining attached to the latter. The great stability of methyl benzoate rendered it likely that in methyl toluate the ester grouping might prove more resistant than the methyl radicle, and this anticipation was realised, the product being methyl diphenylethane-4:4'-dicarboxylate, accompanied by a little *methyl stilbene-4:4'-dicarboxylate*, m. p. 226—227°, and trioxymethylene. Phenol was strikingly resistant, and after prolonged heating yielded only a small quantity of decomposition products, amongst which benzene and 4-hydroxydiphenyl were present; anisole suffered elimination of the methyl group with formation of phenol, but no trioxymethylene was observed. D. F. T.

Organic Additive Compounds of Potassium Hydroxide. WILLIAM M. DEHN and RUTH E. MERLING (*J. Amer. Chem. Soc.*, 1917, **39**, 2646—2657).—When benzoic acid and potassium hydroxide are brought together in anhydrous ether, the following successive additions and decompositions are recognised:

$$2Ph \cdot CO_2H + 2KOH \longrightarrow CPh(OH)_2 \cdot O \cdot COPh \longrightarrow$$
$$(I.)$$
$$CPh(OH_2) \cdot O \cdot CPh(OH) \cdot OK \longrightarrow 2Ph \cdot CO_2K + 2H_2O.$$
$$(II.) \qquad\qquad (III.)$$
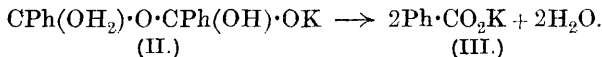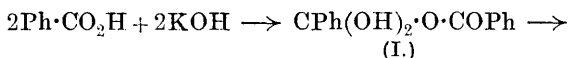
When benzoic anhydride is used in place of benzoic acid, the final salt (III) is the same as in the previous case, but an intermediate salt different from that (II) in the first case is formed,

$$COPh \cdot O \cdot COPh \longrightarrow COPh \cdot O \cdot CPh(OH) \cdot OK \longrightarrow$$
$$O[CPh(OH) \cdot OK]_2 \longrightarrow 2Ph \cdot CO_2K + 2H_2O.$$
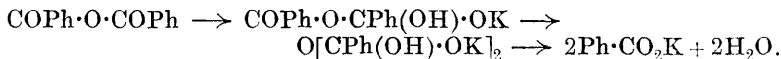
A number of other acids were studied and salts were obtained, the molecular proportions of acid and potassium hydroxide reacting being either 2:1, or 1:1, or 1:2. All these salts, when first formed, were additive compounds, but later they might or might not yield the simple anhydrous salt. Initially, all the water was found to be present in the precipitate, and the progressive loss of water from the precipitate was studied in most cases. That the intermediate compounds were additive was also indicated by the fact that the final anhydrous salts did not take up a molecule of water from an ethereal solution of it. This formation of additive compounds with potassium hydroxide is not peculiar to organic acids, but is common to all organic compounds containing carbonyl groups. The types of compounds studied were acids, acid anhydrides, aldehydes, ketones, esters, amides, imides, alcohols and phenols, and certain miscellaneous compounds. A few oxygen-containing compounds, such as raffinose, saccharin, and camphor, failed to show any reaction with potassium hydroxide. W. G.

New Method of Preparing Aromatic Nitriles by Catalysis.

ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 36—38).—When an
ester of an organic acid is treated with ammonia, it is decomposed,
yielding the alcohol and the amide of the acid, and the latter, on
dehydration, gives the nitrile. The reactions may be effected
simultaneously by passing the vapour of an ester of an aromatic
acid, mixed with gaseous ammonia, over heated thoria at
450—470° (temperature measured in the channel supporting the
catalysis tube). At the latter temperature the reaction is practic-
ally complete, and good yields of benzonitrile are obtained from
methyl-, ethyl-, and *iso*propyl-benzoates. The liquid product of
the reaction separates into two layers, the oily layer consisting
almost entirely of benzonitrile, which is purified by rectification
(b. p. 189—191°). Aldehydic products and gases consisting of
hydrogen and olefines are derived from the alkyl group of the ester.
The nitriles of *o*- and *p*-toluic acids may be prepared in exactly
the same way, and phenylacetonitrile is obtained from ethyl phenyl-
acetate. The method appears to be of general application and
gives good yields.   J. F. B.

Amides, Carbamido-compounds, and Carbamides containing an Aromatic Nucleus.

WALTER A. JACOBS and
MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1917, **39**,
2418—2443. Compare A., 1917, i, 552, 559, 695).—A large
number of compounds of the above classes are described. These,
and similar substances mentioned in the earlier papers, have been
collected as intermediate material in another investigation, of
which an early account is promised.

A. AMIDES. (a) *Amides of Substituted Benzoic Acids.*—
3-*Amino*-6-*hydroxybenzamide* is best obtained by the action of
aqueous ammonia at 110° on methyl aminosalicylate; it crystallises
in silky needles, m. p. 194—197° (decomp.), and gives 3-*chloro-
acetylamino*-6-*hydroxybenzamide*, very pale purple platelets, m. p.
225—227°, when treated by the method already described (*loc. cit.*,
552). Six other amides of this series have been mentioned
previously.

(b) *Amides of Aminophenylacetic Acids.*—*Methyl* m-*amino-
phenylacetate hydrochloride* crystallises in long, thin, glistening
plates, m. p. 167—170° (decomp.); m-*aminophenylacetamide* forms
transparent prisms, m. p. 164—166° (corr.); and m-*chloroacetyl-
aminophenylacetamide* separates in prismatic needles, m. p.
187—188°. (For the parent acid and amides of the para-series,
loc. cit.)

(c) *Derivatives of the Aminophenoxyacetamides.*—o-*Nitrophen-
oxyacetamide*, glistening needles, m. p. 194·5—195·5° (corr.), yields
o-aminophenoxyacetic anhydride when treated with ferrous sulphate
and ammonia. o-*Chloroacetylaminophenoxyacetic acid*,

$$CH_2Cl \cdot CO \cdot NH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2H,$$
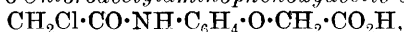
crystallises with $2H_2O$, which it loses at 110°/vac., and then melts
at 144·5—145·5° (corr.); the acid *chloride* forms colourless plates,
m. p. 52—59°, and the *amide* crystallises in needles, m. p.

158—161°. m-*Aminophenoxyacetamide*, from the ethyl ester, forms delicate, cream-coloured needles, m. p. 123·5—124° (corr.), and yields m-*chloroacetylaminophenoxyacetamide*, radiating masses of minute leaflets, m. p. 235—238° (decomp.). p-*Aminophenoxyacetamide* crystallises in creamy prisms, m. p. 127·5—128·5°, and the *chloroacetyl* compound separates in colourless needles, m. p. 195—196·5° (corr.), and forms a *hexamethylenetetraminium* salt, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NH_2,C_6H_{12}N_4$. p-*Nitrophenoxyacetyl chloride* crystallises in hexagonal tablets, m. p. 86—87° (corr.); p-*nitrophenoxyacetomethylamide* forms brilliant needles, m. p. 165·6° (corr.); and p-*aminophenoxyacetomethylamide*,

$$NH_2\cdot C_6H_4\cdot O\cdot CH_2\cdot CO\cdot NHMe,$$
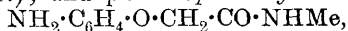
separates in creamy needles, m. p. 109·5—111° (corr.). The following 4-*aminophenoxyacetamides* are obtained from the corresponding esters : 2-*methyl*-, long, flat, glistening needles, m. p. 155·5—156° (corr.); 3-*methyl*-, very pale pink, filamentous masses, m. p. 136—137°; 2:5-*dimethyl*-, silky needles, m. p. 153—154° (corr.); 2-*methyl*-5-iso*propyl*-, diamond-shaped plates, m. p. 108—109° (corr.); 3-*methyl*-6-iso*propyl*-, pointed leaflets, m. p. 125—125·5° (corr.); 2-*bromo*-, masses of long, creamy needles, m. p. 159—160° (corr.); 6-*methoxy*-, glistening needles, m. p. 177·5—178·5° (corr.); 6-*carbethoxy*-, minute leaflets, m. p. 135—136° (corr.); 6-*acetyl*-, brownish-yellow leaflets, m. p. 138—139°. Colour reactions with ferric chloride and R-salt (after diazotisation) are described for most of these compounds. (For the parent acids or esters, *loc. cit.*)

(d) *Derivatives of Aminobenzenesulphonamides.*—Aniline-m-sulphonic acid is dissolved in an equivalent of *N*-sodium hydroxide, shaken with acetic anhydride, the solution evaporated under reduced pressure, and the sodium m-acetylaminobenzenesulphonate left is triturated with phosphorus pentachloride. The crude sulphonyl chloride so formed is treated with ammonia, and so converted into m-*acetylaminobenzenesulphonamide*, minute rhombs, m. p. 216—219°. This is hydrolysed by hydrochloric acid to the known m-aminobenzenesulphonamide, which forms a *chloroacetyl* compound, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot SO_2\cdot NH_2$, aggregates of minute needles, m. p. 165° (clear). Sodium sulphanilate is acetylated in the same way, and finally converted into p-*chloroacetylaminobenzenesulphonamide*, needles, m. p. 215—217°.

B. CARBAMIDES. (a) *Carbamides of Substituted Benzoic Acids.*—o-Aminobenzoylcarbamide (*loc. cit.*) gives o-*chloroacetylaminobenzoylcarbamide*, long, glistening needles, m. p. 222—223° (decomp.), and m-aminobenzoylcarbamide yields the *chloroacetyl* compound, slender needles, decomp. 252—253°. p-*Nitrobenzoylcarbamide*, microscopic prisms, m. p. 243—245°, gives rise to p-*aminobenzoylcarbamide*, minute plates, partly decomposed, but not molten, at 285°, and p-*chloroacetylaminobenzoylcarbamide*, decomp. 275—280°. o-*Hydroxybenzoylcarbamide* (*salicoylcarbamide*), microscopic, pale yellow crystals, m. p. 184—186° (decomp.), is obtained by the interaction of carbamide and o-acetoxybenzoyl

chloride in benzene, followed by agitation of the acetyl derivative with cold sodium hydroxide. m(?)-*Chloroacetylaminomethyl-benzoylcarbamide*, $CH_2Cl\cdot CO\cdot NH\cdot CH_2\cdot C_6H_4\cdot CO\cdot NH\cdot CO\cdot NH_2$, a microcrystalline powder, m. p. 225—228° (decomp.), is obtained by the action of methylolchloroacetamide on benzoylcarbamide in sulphuric acid solution (compare Einhorn, A., 1906, i, 245).

(b) *Derivatives of Phenylacetylcarbamide.*—Phenylchloroacetyl chloride and carbamide yield α-*chlorophenylacetylcarbamide*, $CHPhCl\cdot CO\cdot NH\cdot CO\cdot NH_2$, needles, m. p. 198°. p-*Nitrophenyl-acetylcarbamide*, hair-like needles, m. p. 250—252° (decomp.), gives p-*aminophenylacetylcarbamide*, felted needles, m. p. 198—199° (evolution of gas), and p-*chloroacetylaminophenylacetylcarbamide*, m. p. 241° (decomp.).

(c) *Derivatives of Aminophenoxyacetylcarbamides.*—o-*Nitro-phenoxyacetyl chloride*, long, silky, yellow needles, m. p. 41—42° (corr.), gives o-*nitrophenoxyacetylcarbamide*, cream-coloured, irregular prisms, m. p. 186—188°, which is easily hydrolysed, even by ammonia. p-*Nitrophenoxyacetylcarbamide*, m. p. 250° (decomp.), yields p-*aminophenoxyacetylcarbamide*, long needles, which melt at 198—199°, give off a gas, resolidify, and melt again, evolving gas, at above 240°, and p-*chloroacetylaminophenoxyacetyl-carbamide*, minute, flat needles, m. p. 238—240° (decomp.). A better yield of this compound is obtained from the corresponding acid chloride and carbamide. p-*Chloroacetylaminophenoxyacetic acid*, from the aminophenoxyacetic acid, crystallises in rosettes of soft needles, with $1CH_3\cdot CO_2H$, m. p. 170° (free from solvent of crystallisation); the *chloride*, $CH_2Cl\cdot CO\cdot NH\cdot C_6H_4\cdot O\cdot CH_2\cdot COCl$, forms aggregates of platelets, m. p. 147—152° (decomp.), and the *methyl* ester forms flat needles, m. p. 170—173°.

C. AROMATIC CARBAMIDES CONTAINING AN AMIDO-GROUP.—These carbamido-amides are generally prepared by the action of potassium cyanate on acetic acid solutions of the amino-amides. o-*Carb-amidobenzamide*, $NH_2\cdot CO\cdot NH\cdot C_6H_4\cdot CO\cdot NH_2$, crystallises in stout, cream-coloured, hexagonal plates, which melt at 184—185°, evolving ammonia, and changing thereby into solid benzoylenecarbamide; m-*carbamidobenzamide* forms flat needles, m. p. 235° (decomp.; resolidification), and gives m-*chloroacetylcarbamidobenzamide*, decomp. 223—224°. p-*Carbamidobenzamide* forms aggregates of prisms, m. p. 240—242° (gas evolved; resolidifies; continues to evolve gas; finally molten at 275°), and yields a *chloroacetyl* compound, hexagonal plates, decomp. 236—237°. m-*Carbamidophenyl-acetamide*, m. p. 201—202°, gives a *chloroacetyl* compound,

$$CH_2Cl\cdot CO\cdot NH\cdot CO\cdot NH\cdot C_6H_4\cdot CH_2\cdot CO\cdot NH_2,$$
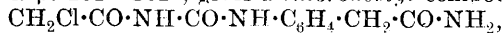
very pale pink aggregates of platelets and needles, m. p. 179—181° (decomp.). p-*Carbamidophenylacetamide* forms rectangular plates, m. p. 233—236° (decomp.; resolidification), and gives a *chloro-acetyl* compound, m. p. 200—201° (decomp.). p-*Carbamidophen-oxyacetamide* crystallises in radiating masses of long, flat, pale brown needles, m. p. 230° (evolution of gas; resolidification; second m. p 260°), and its *chloroacetyl* compound decomposes at 230°.

Methyl p-*carbamidophenoxyacetate*, m. p. 192—193°, gives a *chloroacetyl* compound,

$$CH_2Cl \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot O \cdot CH_2 \cdot CO_2Me,$$
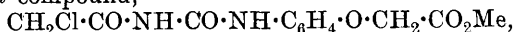
flat prisms, m. p. 181—183° (decomp.).

D. CARBAMIDES WITH OTHER SUBSTITUENTS AND SIDE CHAINS.— p-Hydroxyphenylcarbamide yields p-*chloroacetylcarbamidophenyl chloroacetate*, needles and long, thin plates, m. p. 185·5—187·5°, when boiled with chloroacetyl chloride and benzene; p-*acetylcarbamidophenyl acetate*, delicate, pale pink needles, m. p. 213·5—214° (corr.), when warmed with acetic anhydride and a little sulphuric acid; and p-*carbamidophenyl acetate*, m. p. 201—202·5°, when treated with acetyl chloride and pyridine. The latter may be chloroacetylated; p-*chloroacetylcarbamidophenyl acetate*,

$$CH_2Cl \cdot CO \cdot NH \cdot CO \cdot NH \cdot C_6H_4 \cdot OAc,$$
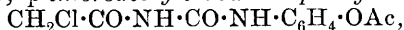
forms spindles and plates, m. p. 181—182·5° (corr.).

p(?)-*Carbamidochloroacetylbenzylamine*,

$$NH_2 \cdot CO \cdot NH \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot CO \cdot CH_2Cl,$$
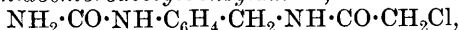
microscopic spears, m. p. 173—174°, is obtained by the action of methylolchloroacetamide on phenylcarbamide (Einhorn's method, *loc. cit.*).

p(?)-*Carbamidophenyl chloromethyl ketone*, creamy, nacreous plates, m. p. 197—198° (decomp.), is prepared by the condensation of phenylcarbamide and chloroacetyl chloride under the influence of aluminium chloride.

p-Acetylaminophenoxyethyl bromide is readily hydrolysed by hydrobromic acid to β-*bromoethoxyaniline hydrobromide*, thin plates, m. p. 227—228° (gas evolution). The free *base* (described as p-*aminophenoxyethyl bromide*) crystallises in minute, glistening platelets, m. p. 83—84·5°, decomp. 260°, and the crude salt reacts with potassium cyanate to give β-*bromoethoxyphenylcarbamide* (p-*carbamidophenoxyethyl bromide*), m. p. 160—162°. J. C. W.

The Behaviour of the Alkali Salts of the Polyhydroxy-benzoic Acids at Higher Temperatures. DANICA MRAZEK

(*Monatsh.*, 1917, **38**, 211—218).—The alkali salts of the dihydroxy- and trihydroxy-benzoic acids when heated at 200—300° do not undergo intramolecular rearrangement, and therefore do not behave like the potassium and thallium salts of salicylic acid, which give rise to the p-hydroxybenzoates, but resemble more closely the salicylates of sodium, lithium, and the alkaline earth metals, which undergo decomposition with formation of carbon dioxide and phenol. In an examination of the behaviour of the potassium salts of α- and β-resorcylic acids, protocatechuic acid, gentisic acid, gallic acid, and pyrogallolcarboxylic acid, it was found that carbon dioxide was generally liberated below 300°, whilst in the case of β-resorcylic acid, protocatechuic acid, and gallic acid a partial further substitution of carbon dioxide into the molecule, with formation of the corresponding polyhydroxyphthalic acid, was also observed. The lithium salt of β-resorcylic acid behaved similarly to the potassium salt, but with the sodium salt the formation of

dicarboxylic acid was negligble, and an amorphous *substance*, $C_{12}H_{10}O_3$, was obtained. With the sodium salt of protocatechuic acid no formation of a dicarboxylic acid was observable.

D. F. T.

The *cyclo*Propane Series. III. E. P. KOHLER, G. A. HILL, and L. A. BIGELOW (*J. Amer. Chem. Soc.*, 1917, **39**, 2405—2418. Compare A., 1917, i, 566—570).—In the earlier papers, three reactions of *cyclo*propane derivatives were described which involved rupture of the ring in the three possible ways, but the primary effect of some of the reagents could only be surmised. New compounds of this series have therefore been sought out in the hope of isolating from them definite products to fill the gaps in the chain of evidence, and a certain measure of success has been achieved.

Experiments with 3-p-*Bromobenzoyl-2-phenyl*cyclo*propane*-1:1-*dicarboxylic Acid.*—*p*-Bromophenyl styryl ketone condenses with the malonic esters under the influence of the sodium alkyloxides to give the *methyl* ester (needles, m. p. 96°) and *ethyl* ester (m. p. 75—76°) of γ-*p-bromobenzoyl-β-phenylethylmalonic acid*,

$$C_6H_4Br \cdot CO \cdot CH_2 \cdot CHPh \cdot CH(CO_2H)_2, H_2O,$$
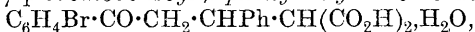
which . crystallises in transparent plates. The methyl ester yields *methyl γ-bromo-γ-p-bromobenzoyl-β-phenylethylmalonate* on bromination; this exists in plates, m. p. 98°, and needles, m. p. 113°, which are separated after many crystallisations from methyl alcohol. The condensation of this compound to *methyl* 3-*p-bromobenzoyl-2-phenyl*cyclo*propane*-1:1-*dicarboxylate* proceeds smoothly. Two forms are produced; with magnesium methoxide, both bromocompounds yield a product which crystallises in thin plates, m. p. 104°, whilst with potassium acetate and boiling methyl alcohol, both bromides give an isomeride which separates in compact tablets, m. p. 113°; the former is converted into the latter by boiling with methyl alcohol and a trace of an acid.

As usual with these compounds, the ring is opened between 1 and 3 by treatment with zinc dust and acetic acid, the product being the above methyl ester, m. p. 96°. Similarly, alkaline agents effect hydrolysis and also open the ring between 1 and 2. With sodium alkyloxides in moist ether, however, it is possible to control hydrolysis so that the *methyl hydrogen* ester (plates, m. p. 175—176°) and *ethyl hydrogen* ester (small tablets, m. p. 144°; the diethyl ester is not described) are produced. The ethyl hydrogen ester is the best material for the final hydrolysis, by the ordinary methods, to the free acid, and it may be prepared from the original ketone and ethyl malonate in a day or so without purifying the intermediate products. 3-*p-Bromobenzoyl-2-phenyl*cyclo*propane*-1:1-*dicarboxylic acid* crystallises with $1H_2O$ or $1Et_2O$, and changes on heating at 160—180° into β-*p-bromobenzoyl-γ-phenylbutyrolactone*,

$$(CO_2H)_2C{<}{\overset{CHPh}{\underset{CH \cdot CO \cdot C_6H_4Br}{|}}} \longrightarrow C_6H_4Br \cdot CO \cdot CH{<}{\overset{CHPh \cdot O}{\underset{CH_2 - CO}{|}}},$$
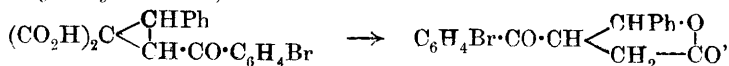
which crystallises in needles, m. p. 116°, together with a trace of *α-benzylidene-γ-p-bromophenylcrotonolactone*, lemon-yellow plates, m. p. 180—183°. The butyrolactone is converted into *β-p-bromobenzoyl-γ-phenyl*isocrotonic *acid*, $CHPh:C(CO \cdot C_6H_4Br) \cdot CH_2 \cdot CO_2H$, m. p. 156°, when shaken with just sufficient sodium methoxide in ether. This unsaturated acid yields *methyl γ-bromo-β-p-bromobenzoyl-γ-phenylbutyrate*, $CHPhBr \cdot CH(CO \cdot C_6H_4Br) \cdot CH_2 \cdot CO_2Me$, m. p. 140° (decomp.), when esterified by means of hydrobromic acid; the same ester is also obtained by similar treatment of the butyrolactone. The substituted *iso*crotonic acid also gives benzaldehyde and *β-p-bromobenzoylpropionic* acid, thin plates, m. p. 140°, when treated with alkalis, so these are the products if the butyrolactone is left in contact with alkaline agents in excess.

3-*p*-Bromobenzoyl-2-phenyl*cyclo*propane-1 : 1-dicarboxylic acid also reacts with hydrogen bromide in acetic acid, yielding *γ-bromo-β-p-bromobenzoyl-γ-phenylethylmalonic acid*,

$$CHPhBr \cdot CH(CO \cdot C_6H_4Br) \cdot CH(CO_2H)_2,$$
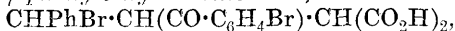
which separates in stout needles, and crystallises from ether in lustrous plates containing combined solvent. This acid suffers loss of hydrogen bromide when shaken with magnesium acetate in dry ether, with the formation of *α-carboxy-β-p-bromobenzoyl-γ-phenylbutyrolactone*, $O{<}^{CO---CH \cdot CO_2H}_{CHPh \cdot CH \cdot CO \cdot C_6H_4Br}, H_2O$, in small, flattened needles, which readily change on heating into the above butyrolactone, m. p. 116°. The *methyl* ester, plates, m. p. 104°, is easily obtained from the *cyclo*propane acid directly. A small quantity of *β-bromo-β-phenyl-β'-p-bromobenzoyldimethylmalonic acid*,

$$CHPhBr \cdot C(CO_2H)_2 \cdot CH_2 \cdot CO \cdot C_6H_4Br,$$
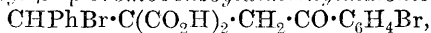
is also formed by the action of hydrogen bromide on the *cyclo*propane acid. It crystallises in plates.

When the *cyclo*propane acid methyl ester is left with magnesium methoxide, the ring is ruptured between 1 and 2, and *methyl β-p-bromobenzoyl-γ-phenylvinylmalonate*,

$$CHPh:C(CO \cdot C_6H_4Br) \cdot CH(CO_2Me)_2,$$
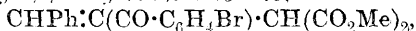
is formed; this crystallises in needles, m. p. 104°, which change into a stereoisomeride (hard, lustrous prisms, m. p. 92—93°) when left with hydrochloric acid.

*Experiments with Benzoyl-*m-*nitrophenylcyclopropanedicarboxylic Acid.*—*m*-Nitrostyryl phenyl ketone and the malonic esters react to form *methyl γ-benzoyl-β-m-nitrophenylethylmalonate*, short needles with ½MeOH. m. p. 92°, or silky needles, m. p. 102°, and the *ethyl* ester, m. p. 100—100·5°. These yield the corresponding *γ-bromo*-esters, $COPh \cdot CHBr \cdot CH(C_6H_4 \cdot NO_2) \cdot CH(CO_2R)_2$; each exists in two forms, the methyl ester in long, silky needles, m. p. 149·5°, and short, lustrous needles, m. p. 129·3°; the ethyl ester in short, brittle needles, m. p. 101°, and soft, slender needles or hard prisms, m. p. 98·5°. These bromo-esters are condensed to *cyclo*propane derivatives by the usual mild agents, as above. The following esters are mentioned: *methyl 3-benzoyl-2-m-nitrophenyl-*

cyclo*propane*-1 : 1-*dicarboxylate*, stable, large, prismatic plates, m. p. 109·3°, and labile, slender needles, m. p. 111·5°; the *methyl hydrogen* ester, short, hard prisms, m. p. 154·5°; and the *ethyl* ester, small plates, m. p. 67°. The methyl hydrogen ester is hydrolysed by the prolonged action of alcoholic potassium hydroxide to 3-*benzoyl*-2-m-*nitrophenyl*cyclo*propane*-1 : 1-*dicarboxylic acid* (I), which crystallises with $1H_2O$ in lustrous plates, and decomposes at above 135° into α-m-*nitrobenzylidene*-γ-*phenylcrotonolactone* (II),

(I) $(CO_2H)_2C{<}{\overset{\text{CH·C}_6\text{H}_4\text{·NO}_2}{\underset{\text{CHBz}}{}}}$ (II) $NO_2\text{·}C_6H_4\text{·CH:}C{<}{\overset{\text{CH:CPh}}{\underset{\text{CO–O}}{}}}$,
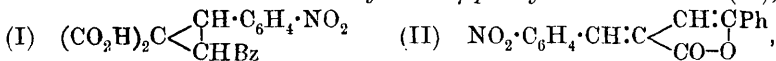
small, yellow plates, m. p. 208°, and β-*benzoyl*-β-m-*nitrobenzylidene*-*propionic acid*, $NO_2\text{·}C_6H_4\text{·CH:CBz·CH}_2\text{·CO}_2H$, slender needles, m. p. 172°. Syntheses of these products are also described.

The cyclopropane methyl ester, m. p. 109·5°, yields *methyl* β-*benzoyl*-β-m-*nitrobenzylidenemethylmalonate*,

$$NO_2\text{·}C_6H_4\text{·CH:CBz·CH(CO}_2\text{Me})_2.$$

prisms, m. p. 139·5°, when boiled for a long time with magnesium methoxide solution; this ester gives m-nitrobenzoic acid when oxidised with permanganate in aqueous acetone, but a compound, m. p. 197°, of undetermined structure is formed in dry acetone.

J. C. W.

4 : 4'-Dimethylbenzophenone and its Condensation with Phenol. M. GOMBERG and J. D. TODD (*J. Amer. Chem. Soc.*, 1917, **39**, 2392—2396).

—Toluene and carbon tetrachloride condense under the influence of aluminium chloride to give a mixture of ditolylmethylene dichlorides, which suffer violent decomposition when distillation is attempted. On hydrolysis, the mixture gives a 30—35% yield of di-*p*-tolyl ketone, m. p. 93°, and an oily residue of other tolophenones, soluble in light petroleum. The pure ketone reacts with phosphorus pentachloride at 100° to form di-*p*-tolyl-methylene dichloride, as a mobile, green liquid, which decomposes at above 175°. This behaves like diphenylmethylene dichloride towards phenol (A., 1916, i, 29), giving diphenoxydi-*p*-tolyl-methane, m. p. 132—133°, if the agents are diluted with benzene, or p-*hydroxyphenyldi*-p-*tolylcarbinol* if no diluent is used. Two forms of this carbinol are described, but no suitable medium for crystallisation has been found. The *benzenoid* form,

$$OH\text{·}C_6H_4\text{·}C(C_6H_4Me)_2\text{·}OH,$$
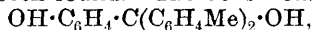
obtained by precipitation with carbon dioxide from a solution in sodium hydroxide, is pale yellow, turns red and melts at about 70°, and evolves water at 125°; the *quinonoid* form,

$$(OH)_2\text{:}C_6H_4\text{:}C(C_6H_4Me)_2,$$
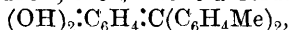
obtained by pouring an acetic acid solution into water, is orange-red, becomes dark red and melts at about 65°, and freely gives off water at above 90°.   J. C. W.

The Action of Phosphorus Trichloride on Unsaturated Ketones. JAMES B. CONANT (*J. Amer. Chem. Soc.*, 1917, **39**, 2679—2684).

—Phosphorus trichloride reacts with αβ-unsaturated ketones in glacial acetic acid solution, and on diluting the products

with water, β-ketonic phosphonic acids are obtained. It is best to allow the reaction mixture to remain overnight before diluting it with water. In this way, phenyl *p*-methoxystyryl ketone yields *β-benzoyl-α-4-methoxyphenylethylphosphonic acid*,

$$OMe \cdot C_6H_4 \cdot CH(PO_3H_2) \cdot CH_2 \cdot COPh,$$
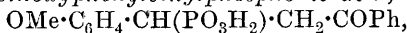
m. p. 189°, giving an *oxime*, m. p. 156° (decomp.), a crystalline *sodium* salt, soluble *calcium* and *barium* salts, and insoluble *silver* and *lead* salts. Phenyl styryl ketone yields *β-benzoyl-α-phenylethylphosphonic acid*, m. p. 116°, and distyryl ketone yields *β-cinnamoyl-α-phenylethylphosphonic acid*,

$$PO_3H_2 \cdot CHPh \cdot CH_2 \cdot CO \cdot CH{:}CHPh.$$
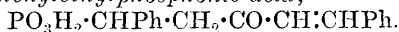
W. G.

Bromohydroxynaphthaquinones.   A. S. WHEELER and V. C. EDWARDS (*J. Amer. Chem. Soc.*, 1917, **39**, 2460—2468. Compare A., 1916, i, 392).—1 : 4 : 5 : 6-Tetrahydroxynaphthalene is an interesting compound, since it appears to exist in only one form, but reacts sometimes as a tetrahydric phenol and sometimes as a quinone. The bromination of the compound, and also of its oxidation product, naphthazarin, in the cold has now revealed another curious type of isomerism. Both substances yield quinone dibromides, thus:

Naphthazarin —→ " α- " m. p. 151—152°   Tetrahydroxynaphthalene.
                   " β- " m. p. 180°   ←—   Quinone form.
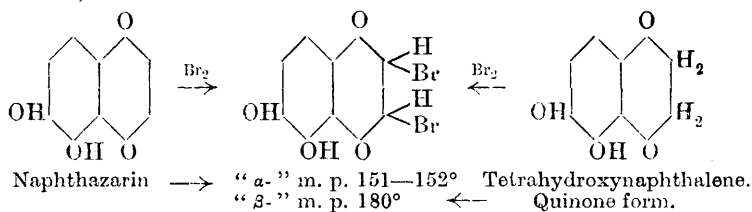
but the two products are not identical and not interchangeable, although they are isomeric and yield the same derivatives on treatment with alcohol, which removes the elements of hydrogen bromide. It may be that in one, both bromine atoms are outside the ring and the hydrogen atoms within, whilst in the other form a different spatial arrangement is observed.

Naphthazarin reacts with bromine in cold chloroform to give the " α "-form of 5 : 6-*dihydroxy*-1 : 4-*naphthaquinone* 2 : 3-*dibromide*, crystallising in lemon-yellow prisms, which become red and then grey between 135° and 150°, and have m. p. 151—152°. This loses hydrogen bromide when warmed with alcohol, giving 2(or 3)-*bromo*-5 : 6-*dihydroxy*-1 : 4-*naphthaquinone*, in reddish-brown prisms, m. p. 188—189° (after giving a coloured vapour at 170°), and yields the tetrahydroxynaphthalene on reduction with stannous chloride. It also forms a *diacetate*, $C_{14}H_{10}O_4Br_2$, when boiled for a long time with acetyl chloride. This crystallises in colourless plates, which turn red at 110° and melt at 166—167°, and also become deep red when kept, and it reacts with alcohol to form the *diacetate* of the monobromo-compound, bright yellow, silky needles, m. p. 191—192°, which may be obtained also by direct acetylation.

Naphthazarin yields 5 : 6-diacetoxy-1 : 4-naphthaquinone, m. p. 189—190°, when boiled with acetyl chloride, but the tetra-acetoxy-naphthalene, m. p. 277—279°, is formed if acetic anhydride is applied (compare Zincke and Schmidt, A., 1895, i, 613). The diacetate yields 1 : 4-*dihydroxy-*5 : 6-*diacetoxynaphthalene* on reduction with stannous chloride; this forms colourless, microscopic plates, which turn red at 230° and have m. p. 241—243°.

Tetrahydroxynaphthalene reacts with bromine in cold acetic acid to form the "β"-*modification* of 5 : 6-dihydroxy-1 : 4-naphthaquinone 2 : 3-dibromide. This crystallises in lemon-yellow prisms, which begin to turn red at 140° and have m. p. 180°. It loses hydrogen bromide in the sunlight, becoming steely-blue, and it yields all the products described above in connexion with the α-isomeride.

If tetrahydroxynaphthalene is brominated in acetic acid at 70°, the product is 2 : 3-*dibromo-*5 : 6-*dihydroxy-*1 : 4-*naphthaquinone* (annexed formula); this crystal-lises in red leaflets, m. p. 258°, and yields a 5 : 6-*diacetate*, yellow needles, m. p. 200—201°, which may be reduced to 2 : 3-*dibromo-*1 : 4-*dihydroxy-*5 : 6-*diacetoxynaphthalene*, colourless needles, m. p. 196—197°, by means of stannous chloride.

The many inter-reactions which have been established among these compounds are illustrated by a chart of formulæ.

J. C. W.

Oil of Artemisia Annua. K. ASAHINA and YOSHITOMI (*J. Pharm. Soc. Japan*, 1917, 424, 1; *Perf. Ess. Oil Rec.*, 1917, **8**, 353—354).

—Oil of *Artemisia annua* was freed from aldehydic constituents, distilled with steam, and fractionated. The lower fractions contained cineole and the higher *l*-camphor. The fraction boiling between 181° and 190°/10 mm. contained a new *ketone*, $C_{10}H_{16}O$, b. p. 182°, D_4^{14} 0·8906, $n^{18·5}$ 1·4695, mol. refraction 47·57 (calc., 47·45), yielding a *semicarbazone*, m. p. 95—96°. Reduction by means of hydrogen in presence of platinum converted the ketone into *tetrahydro-artemisia ketone*, $C_{10}H_{20}O$, b. p. 73°/15 mm., 173°/760 mm., $D_4^{19·5}$ 0·8262, n_D 1·42425, yielding a *semicarbazone*, m. p. 134—135°. (See also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.)

T. F. B.

Constituents of Formosan Lemongrass Oil. KINZO KAFAKU (*J. Chem. Ind. Tōkyō*, 1917, **20**, 825—833).

—Formosan lemongrass oil contains an olefinic terpene which yields dihydro-myrcene and 2 : 6-dimethyloctane on treatment with hydrogen under different conditions, and succinic and oxalic acids on oxidation; it is therefore believed to be myrcene. The oil also contains an aldehydic substance other than citral, which, however, has not been isolated. (See also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.)

T. F. B.

Action of Alkyl Nitrites on Pyrrole. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 127—131).—The action of ethyl nitrite on pyrrole in the presence of sodium ethoxide at 5—10° results in the production of nitrosopyrrole-black (A., 1917, i, 413) and the *ethyl* ester of the *oxime* of *maleinimide*,

$$\text{OH·N:C--NH} >\text{CO,} \atop \text{CH:CH}$$
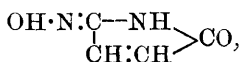
which forms colourless needles, m. p. about 100°. This compound is hydrolysed by water, acids, or alkalis with formation of the *oxime*, $C_4H_4O_2N_2$, which decomposes at 195° and melts at 205°. The oxime forms a *sodium* salt, $C_4H_3O_2N_2Na$, which when treated with ethyl iodide yields a derivative isomeric with the ethyl ester above described; it crystallises in pale yellow needles m. p. 55—60°. The oxime of maleinimide when treated with bromine yields fumaric acid and monobromomaleinimide.   R. V. S.

Betaines and Alkyliodides. R. VON WALTHER and ALBERT B. WEINHAGEN (*J. pr. Chem.*, 1917, [ii], **96**, 50—58).— α-Chlorophenylacetic acid reacts normally with quinoline, giving rise to a betaine additive *compound* of the formula $C_{17}H_{14}O_2NCl$ (*mercurichloride*, m. p. 140°; *perchlorate*, decomp. at 120°), but with pyridine, α-picoline, and nicotine the additive process is complicated by the liberation of carbon dioxide, the products respectively being benzylpyridinium chloride, *benzylpicolinium chloride* (*aurichloride*, m. p. 133—134°; *platinichloride*, m. p. 212—213°; *dichromate*, m. p. 129°), and *benzylnicotinium chloride*, decomp. at 236° (*diaurichloride*, decomp. at 178°; *picrate*, decomp. at 99°). With quinaldine and *s*-collidine, however, no additive product is obtained, probably owing to steric hindrance, but the latter base, presumably on account of its greater basicity, extracts hydrogen chloride from the chlorophenylacetic acid. Pyridine and α-chloropropionic acid when heated together give rise to ethylpyridinium chloride (*aurichloride*, m. p. 190° decomp.), carbon dioxide being liberated. With benzyl chloride and nicotine, the monobenzyl- or dibenzyl-nicotinium compound is obtained according to the proportions taken; *dibenzylnicotinium diaurichloride* decomposes at 183° and the *platinichloride* at 211°, whilst the picrate has m. p. 122°.

With *o*-nitrobenzyl chloride, the following products were obtained: *o-Nitrobenzylpyridinium chloride*, $C_{12}H_{11}O_2N_2Cl,1\frac{1}{2}H_2O$, colourless needles, m. p. 103°; *mercurichloride*, leaflets, m. p. 145°; *dichromate*, m. p. 172°; *perchlorate*, with $1H_2O$, m. p. 154°; *platinichloride*, m. p. 223°, decomp. at 228°; *picrate*, needles, m. p. 148°. *o-Nitrobenzyl-α-picolinium chloride*, $C_{13}H_{13}O_2N_2Cl$, m. p. 115°; *aurichloride*, m. p. 132—133°. *o-Nitrobenzylquinolinium chloride*; *dichromate*, carbonises at 190—200°; *mercurichloride*. *o-Nitrobenzylnicotinium chloride*; *platinichloride*, $C_{17}H_{21}O_2N_3PtCl_6$, m. p. 227—229°; *diaurichloride*; *dichromate*, m. p. 110°. No reaction was observable between *o*-nitrobenzyl chloride and collidine,

probably on account of steric hindrance. *m*-Nitrobenzyl chloride in a similar manner was made to yield m-*nitrobenzylpyridinium chloride*, crystalline spangles with $1\frac{1}{2}H_2O$, m. p. 97—99° (*mercurichloride*, needles, m. p. 117—119°; *dichromate*, m. p. 189° decomp.; *perchlorate*, needles, m. p. 142°; *picrate*, needles, m. p. 142°; *platinichloride*, m. p. 213—215°); m-*nitrobenzyl-α-picolinium chloride*, needles, m. p. 118° (*aurichloride*, m. p. 159°); m-*nitrobenzylquinolinium chloride* (*dichromate*, carbonises at 190°; *mercurichloride*); and m-*nitrobenzylnicotinium chloride* (*platinichloride*, m. p. 204—205° decomp.; *aurichloride*, m. p. 185° decomp.). Similarly, *p*-nitrobenzyl chloride yielded p-*nitrobenzylpyridinium chloride*, with $1\frac{1}{2}H_2O$, m. p. 64—66° (*mercurichloride*, needles or tablets, m. p. 137°; *perchlorate*, needles, m. p. 131°; *dichromate*; *picrate*, needles, m. p. 171°; *platinichloride*, spangles, m. p. 210—211°); p-*nitrobenzylnicotinium chloride* (*aurichloride*, decomp. near 80°; *platinichloride*, m. p. 223°); p-*nitrobenzyl-α-picolinium chloride* (*aurichloride*, m. p. 159°; *platinichloride*, needles, m. p. 217°; *mercurichloride*, needles, m. p. 139—140°); and p-*nitrobenzylquinolinium chloride* (*dichromate*, m. p. 176°; *mercurichloride*); 2-methylquinoline and collidine did not form additive compounds with *p*-nitrobenzyl chloride.

Collidine (*perchlorate*, m. p. 233°) when heated with benzaldehyde gives rise to *benzylidenecollidine*, an undistillable oil (*mercurichloride*, m. p. 226°; *platinichloride*, with $1H_2O$, m. p. 236—238°), but no reaction was observable with acetaldehyde, nitrobenzaldehyde, or chloral.

Attempts to prepare alkylaminoacetic acids by the decomposition of pyridinebetaine with the aid of nitric acid or of hydriodic acid and phosphorus were unsuccessful, the only isolated product being pyridine.   D. F. T.

The Esterification of 2 : 4-Lutidinetricarboxylic Acid. ALFRED KIRPAL and KARL REIMANN (*Monatsh.*, 1917, **38**, 249—265. See A., 1906, i, 697; 1907, i, 722).—When 2 : 4-dimethylpyridine-3 : 5 : 6-tricarboxylic acid (2 : 4-lutidinetricarboxylic acid) is esterified by means of alcohol and hydrogen chloride, the sole product is the 6-*ethyl* ester, $C_{12}H_{13}O_6N,2H_2O$, colourless prisms, m. p. 100°, to the formation of which there is least steric hindrance; the constitution of this ester is demonstrated by conversion through the corresponding *amide*, $C_{10}H_{10}O_5N_2$, m. p. 240° (decomp.), into 6-*amino*-2 : 4-*dimethylpyridine*-3 : 5-*dicarboxylic acid*, $C_9H_{10}O_4N_2$, m. p. 242° (decomp.), which on treatment with nitrous acid and heating yields successively 6-*hydroxy*-2 : 4-*dimethylpyridine*-3 : 5-*dicarboxylic acid*, $C_9H_9O_5N,H_2O$, needles, m. p. 232°, and 6-hydroxy-2 : 4-dimethylpyridine (γ-lutidostyril; Hantzsch, A., 1885, 397). If the dimethylpyridinetricarboxylic acid is esterified with alcohol only, the above ester is obtained, together with a small quantity of the isomeric 5-*ethyl* ester, $C_{12}H_{13}O_6N,2H_2O$, colourless prisms, m. p. 80°, and then at 170° (decomp.), the two esters being also obtainable by the action of alcohol on the *anhydride*, rhombic tablets,

m. p. 232° (decomp.), which was produced by heating the dimethyl-pyridinetricarboxylic acid with acetic anhydride. The 6-ethyl ester, unlike the 5-ethyl isomeride, is rapidly hydrolysed by boiling with water, and is inert towards alcoholic hydrogen chloride, whereas the latter ester is converted into the 5:6-*diethyl* ester,

$$C_{14}H_{17}O_6N, H_2O,$$
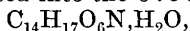
short prisms, m. p. 107°. By heating the ammonium salt of 2:4-dimethylpyridinetricarboxylic acid at 160—170°, it is possible to obtain the *imide*, $C_{10}H_8O_4N_2, H_2O$, m. p. above 300° (decomp.), which when heated in neutral aqueous solution gives the isomeric 5-amide and 6-amide in almost equal quantities.

The electrical conductivity of the 5-ethyl, 6-ethyl, and 5:6-diethyl esters, and of the parent 2:4-dimethylpyridinetricarboxylic acid, was examined in aqueous solution; the acid is a stronger electrolyte than pyridine-2:3:4:5-tetracarboxylic acid.　　　　D. F. T.

Two New Bases from Coal Tar. ALFRED ECKERT and SOPHIE LORIA (*Monatsh.*, 1917, **38**, 225—247).—Weidel and Pick (A., 1885, 556) isolated from bone oil a base which they believed to be 4-methyl-2-ethylpyridine, but the properties of this base when synthesised from γ-picoline and ethyl iodide prove that the base from bone oil was at any rate not pure, and possibly contained no ethyl-substituted pyridine whatever.

Examination of the collidine fraction obtained from coal tar revealed the presence of *s*-trimethylpyridine, 3:5-dimethylpyridine, a small quantity of a collidine, b. p. 165—168°, and of a base giving a picrate, m. p. 114—116°, together with 2:3:6-trimethyl-pyridine and 2:3:4-trimethylpyridine. These two bases have not been found previously in coal tar; the latter has already been pro-duced synthetically (Guareschi, A., 1900, i, 558), whilst the former is now described for the first time. No indication of the presence of any ethyl derivative of pyridine was observed.

2:3:6-*Trimethylpyridine*, $C_5H_2NMe_3$, b. p. 173—174°/734 mm., forms a *platinichloride*, with $1H_2O$, m. p. 250—252° (decomp.), *aurichloride*, needles, m. p. 106°, *picrate*, yellow needles, m. p. 143—144°, and on oxidation yields *pyridine-2:3:6-tricarboxylic acid*, $C_5H_2N(CO_2H)_3, 2H_2O$, m. p. approx. 130°, which at a higher temperature undergoes decomposition into pyridine-2:5-dicarboxylic acid.

2-Methyl-4-ethylpyridine, prepared by the action of ethyl iodide on α-picoline, was found to have b. p. 177—179°/751 mm. (Schultz, A., 1888, 64, gives 169—174°), and to give a platinichloride, yellow cubes, m. p. 203°, and a *picrate*, m. p. 141—142°, whilst the isomeric 2-methyl-6-ethylpyridine obtained in the same reaction had b. p. 160°/747 mm., gave a platinichloride, m. p. 188—190° (decomp.), and a *stannichloride*, m. p. 206—207°; synthetic 4-*methyl-2-ethylpyridine*, b. p. 173—175°/748 mm., yielded a *platinichloride*, m. p. 230°, a *picrate*, m. p. 115—116°, and a *mercurichloride*, m. p. 94—96°.　　　　D. F. T.

A New Synthesis of 2:4-Dioxythiazole and of its 3-Phenyl Derivative. RUDOLPH ANDREASCH (*Monatsh.*, 1917, **38**, 203—209. Compare Andreasch, A., 1880, 877; Andreasch and Zipser, A., 1903, i, 855):—When potassium cyanate is added to a cold aqueous solution of equimolecular quantities of thiolacetic and acetic acids, the potassium salt of carbamylthiolacetic acid, $NH_2 \cdot CO \cdot S \cdot CH_2 \cdot CO_2H$, is produced; on repeated recrystallisation from hot water, this acid undergoes dehydration into 2:4-dioxy-thiazole, $S{<}^{CO-NH}_{CH_2 \cdot CO}$. Phenylcarbimide and thiolacetic acid in ethereal solution react readily, with formation of 2:4-dioxy-3-phenylthiazole, $S{<}^{CO-NPh}_{CH_2 \cdot CO}$, and carbanilide, the formation of the latter being due to the action of water on the phenylcarbimide.

The observed conversion of 3-phenyl*iso*thiohydantoin into 3:4-dioxy-3-phenylthiazole, carbamylthiolacetic acid, thiolacetic acid, and aniline under the influence of mineral acids is probably due to the decomposition following two different courses, one involving mere elimination of the imino-group and the other depending on the disruption of the cyclic molecule; however, the possibility that the phenyl*iso*thiohydantoin contained some of the 2-phenyl isomeride is not excluded.   D. F. T.

Reduction of 4-Anisylidenehydantoin-1-acetic Acid and its Ethyl Ester. DOROTHY A. HAHN and C. PAULINE BURT [with TREAT B. JOHNSON] (*J. Amer. Chem. Soc.*, 1917, **39**, 2468—2472. Compare A., 1917, i, 475).—A variety of products is formed when this acid is reduced with sodium amalgam. Using one equivalent proportion of 2% amalgam and aqueous alcohol as the solvent, and boiling for one hour, keeping the mixture neutral by additions of acetic acid, *sodium 4-anisylidenehydantoin-1-acetate* separates in well-defined, greenish-yellow plates, which become white on dehydration. After boiling for two hours, the salt which separates on cooling in needles is *sodium 4-anisylhydantoin*-1-*acetate*, whilst after boiling with an excess of amalgam, the *disodium* salt, $CO_2Na \cdot CH_2 \cdot NH \cdot CO \cdot NH \cdot CH(CO_2Na) \cdot CH_2 \cdot C_6H_4 \cdot OMe$, is obtained as a crystalline precipitate, which gives the corresponding open-chain acid (*loc. cit.*) on acidifying with hydrochloric acid.

Reduction with zinc and aqueous acetic acid gives a small amount of a *zinc* salt of the formula,

$$\begin{array}{c} NH \cdot CO \cdot NH \cdot CH_2 \cdot CO \cdot O \\ OMe \cdot C_6H_4 \cdot CH{:}C \cdot CO \cdot O \text{———————}Zn \end{array}$$
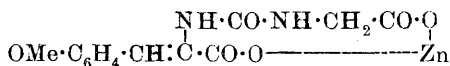
This yields the original 4-anisylidenehydantoin-1-acetic acid on acidifying.

These salts do not melt below 315°, and when they were encountered in the earlier work they were erroneously regarded as a geometric isomeride of the parent acid.   J. C. W.

Pyrimidines. LXXXVI. Production of Glyoxalones by Hydrolysis of Pyrimidine Nucleosides. TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2396—2405. Compare A., 1916, i, 754; 1917, i, 585, 667).—In recent papers, it has been shown that certain hydroxypyrimidine compounds can be converted into glyoxalones merely by hydrolysis with acids; thus, the secondary uracil-nucleoside, 4-a-hydroxyethyl-1 : 2 : 3 : 6-tetrahydropyrimid-2 : 6-dione, yields 4 : 5-dimethylglyoxalone,

$$NH{<}^{CO--CH}_{CO\cdot NH}{>}C\cdot CHMe\cdot OH \xrightarrow{H_2O} CO{<}^{NH\cdot CMe}_{NH\cdot CMe} + CO_2.$$
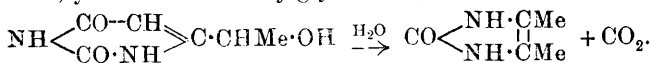
This remarkable reaction presents, therefore, the expulsion of a carbon atom from a 6-membered ring, with the formation of a 5-membered nucleus.

Somewhat analogous reactions of the pyrimidine ring have been known for a long time, but these are the result of oxidation and not mere hydrolysis. Thus, the oxidation in alkaline media of uric acid to allantoin, and of 4-methyluracil to parabanic acid, represent such a removal of a carbon atom. In both cases, the accepted interpretation of the reaction is that given by Behrend, who supposes that the glycols are first produced by oxidation and that subsequent rearrangements take place within these molecules.

Between these glycols and the uracil-nucleosides there is just one feature in common, namely, a hydroxyl group five places removed from the nitrogen atom numbered 1; thus:

$$\begin{array}{ccc}
^{(1)}NH{-}CO^{(6)} & ^{(1)}NH{-}CO & ^{(1)}NH{-}CO \\
| \quad | & | \quad | & | \quad | \\
CO \quad ^{(5)}C(OH)\cdot NH & CO \quad ^{(5)}C(OH)_2 & CO \quad CH \\
| \quad | \qquad {>}CO & | \quad | & | \quad || ^{(5)} \\
NH{-}C(OH)\cdot NH & NH{-}CMe\cdot OH & NH{-}C\cdot CHMe\cdot OH \\
\text{Uric acid glycol.} & \text{Trihydroxydihydro-} & \text{Secondary} \\
 & \text{methyluracil.} & \text{uracil-nucleoside.}
\end{array}$$
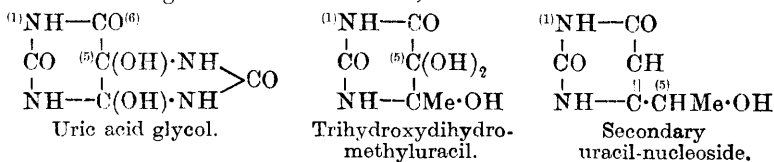
Should the union between the nitrogen atom 1 and carbon atom 6 be broken, for example, by hydrolysis, there would be a hydroxyl group available for a recondensation to a 5-membered ring, and this is the explanation offered of the glyoxalone formation. The following scheme illustrates the probable course of the change:

$$NH{<}^{CO--CH}_{CO\cdot NH}{>}C\cdot CHMe\cdot OH \xrightarrow{+H_2O} \begin{array}{l}NH\cdot CO\cdot NH_2 \\ C(:CH\cdot CO_2H)\cdot CHMe\cdot OH\end{array}$$

$$\downarrow {-CO_2 \atop -H_2O}$$

$$CO{<}^{NH\cdot CMe}_{NH\cdot CMe} \quad \longleftarrow \quad CO{<}^{NH\cdot C:CH_2}_{NH\cdot CHMe}.$$
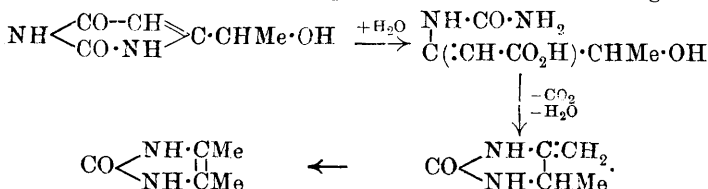
Other activities of the above glycols are discussed; and the trend of future researches in this field is indicated.   J. C. W.

The Decomposition of the Three Ethoxyphenylhydrazines by Hydrochloric Acid. HARTWIG FRANZEN and MORITZ SCHMIDT (*J. pr. Chem.*, 1917, [ii], **96**, 1—25).—It is already known that in

the aminophenylhydrazines the presence of the amino-group reduces the stability of the linking between the two nitrogen atoms (Franzen and von Fürst, A., 1914, i, 206; 1917, i, 58, 59), and the results of the present investigation demonstrate that the ethoxy-radicle exerts a similar but less powerful influence.

p-Ethoxyphenylhydrazine was obtained by Altschul's method; the hydrochloride when pure has m. p. 165° (decomp.); the base yields a *benzylidene* derivative, $C_{15}H_{16}ON_2$, rose-red needles, m. p. 124—125°; a pyruvic acid *derivative*, $OEt \cdot C_6H_4 \cdot NH \cdot N{:}CMe \cdot CO_2H$, yellow needles, m. p. 118°; and a *dibenzoyl* derivative, $C_{22}H_{20}O_3N_2$, colourless needles, m. p. 146°. o-*Ethoxyphenylhydrazine*,

$$OEt \cdot C_6H_4 \cdot NH \cdot NH_2,$$
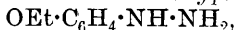
was prepared by converting o-phenetidine into *sodium o-ethoxy-diazobenzenesulphonate*, $OEt \cdot C_6H_4 \cdot N_2 \cdot SO_3Na$, yellow crystals, decomp. with mild explosion at 170°, and reducing this with zinc dust and acetic acid to *sodium o-ethoxyphenylhydrazinesulphonate*, $OEt \cdot C_6H_4 \cdot NH \cdot NH \cdot SO_3Na$, colourless, pearly leaflets, m. p. 205° (decomp.), which on decomposition with aqueous-alcoholic hydro-chloric acid gave the *hydrochloride*, needles, m. p. 159—160° (decomp.), of the desired base; *benzylidene* derivative, $C_{18}H_{18}ON_2$, pale yellow needles, m. p. 98—99°; pyruvic acid *derivative*, $OEt \cdot C_6H_4 \cdot NH \cdot N{:}CMe \cdot CO_2H$, yellow needles, m. p. 138°; *dibenzoyl* derivative, colourless crystals, m. p. 158°. m-Phenetidine, prepared from m-nitroaniline by way of m-nitrophenol and m-nitrophenetole, was, by successive diazotisation and reduction, converted into m-*ethoxyphenylhydrazine*, $OEt \cdot C_6H_4 \cdot NH \cdot NH_2$; *hydrochloride*, colourless; *benzylidene* derivative, colourless needles, m. p. 80°.

When heated with boiling $2N$-hydrochloric acid, o-ethoxyphenyl-hydrazine hydrochloride undergoes decomposition with formation of p-phenetidine, phenetole, p-azophenetole, ethyl chloride, ammonia, and nitrogen, and analogous products, with the exception of the azo-compound, were observed in the decomposition of the ortho-isomeride. The decomposition in each case probably involves a primary formation of chloroamine or of ethoxyphenylchloro-amine produced by the reactions $OEt \cdot C_6H_4 \cdot NH \cdot NH_2 + HCl = OEt \cdot C_6H_4 \cdot NH_2 + NH_2Cl$ and $OEt \cdot C_6H_4 \cdot NH \cdot NH_2 + HCl = OEt \cdot C_6H_4 \cdot NHCl + NH_3$ respectively, the various isolated products resulting from the subsequent reactions of these primary products. By allowing the action of hydrochloric acid on these ethoxyphenyl-hydrazines to occur in the presence of a reducing agent such as stannous chloride, the above concurrent reactions become replaced by the single reaction $OEt \cdot C_6H_4 \cdot NH \cdot NH_2 + 2H = OEt \cdot C_6H_4 \cdot NH_2 + NH_3$, so that the quantity of ammonia formed supplies a convenient measure of the relative rates of the reaction with the ortho-, meta-, and para-compounds. By proceeding in this manner, it is shown that p-ethoxyphenylhydrazine is reduced most rapidly and the meta-isomeride least rapidly, so that the weakening effect of the ethoxy-group in various positions on the stability of the N–N linking falls in the order $p > o > m$, although the influence of the ethoxy-group is much less than that of the amino-group.

The decomposition of the three phenetidines by boiling hydrochloric acid, with formation of ethyl chloride, was also investigated, with the result that the reaction was found to occur most rapidly with *p*-phenetidine and least rapidly with *o*-phenetidine.

D. F. T.

The Nitrogen Distribution in Protalbic and Lysalbic Acids.

CORNELIA KENNEDY and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1917, **39**, 2734—2736).—Lysalbic and protalbic acids have been prepared from egg-albumin by Paal's method (compare A., 1902, i, 653), and their nitrogen distributions have been determined by Van Slyke's method and compared with that of the original albumin, with the following results:

	Percentages in		
	Egg-albumin.	Protalbic acid.	Lysalbic acid.
Ammonia nitrogen	9·08	5·08	8·21
Humin ,,	4·71	4·00	4·49
Cystine ,,	0·72	0·11	0·51
Arginine ,,	6·05	6·32	6·23
Histidine ,,	6·48	7·96	6·42
Lysine ,,	10·09	13·73	12·50
Amino-nitrogen in filtrate from bases	61·26	58·17	58·37
Non-amino-nitrogen in filtrate from bases ...	4·58	5·22	2·70
Total	102·97	100·59	94·43

W. G.

Animal Globulin. I—VI. Confirmed and not Confirmed.

JOHANNES STARKE (*Zeitsch. Biol.*, 1917, **68**, 147—159. Compare A., 1901, i, 242).—The author points out that his views on globulin, based on experiments with ovoglobulin, have since been confirmed by Hekma's work on fibrinogen (A., 1916, i, 513). He also claims priority for the demonstration of the transformation of albumin into globulin, usually ascribed to Moll (A., 1904, i, 356; but see Bywaters and Tasker, A., 1913, i, 1399). H. W. B.

The Effect of Prolonged Acid Hydrolysis on the Nitrogen Distribution of Fibrin with Especial Reference to the Ammonia Fraction.

ROSS AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1917, **39**, 2736—2745).—Fibrin was hydrolysed by boiling with 20% hydrochloric acid for periods of time ranging from one hour to six weeks, and the distribution of nitrogen in the products was determined by Van Slyke's method. The figures for ammonia nitrogen in an acid hydrolysate include not only the amide nitrogen in the protein molecule, but also some ammonia derived from the deamination of certain of the amino-acids. The extent of this deamination depends on the length of hydrolysis, the monoamino-acids being deaminised much more easily than the histone bases. Cystine is not the only amino-acid which undergoes deamination when boiled with hydrochloric acid (com-

pare Van Slyke, A., 1912, i, 735). The figures, in a Van Slyke analysis, for histidine, arginine, and lysine are not appreciably altered by a hydrolysis extending over six weeks, providing that all tryptophan has been so altered that it is not precipitated on the addition of phosphotungstic acid. Increases in the insoluble humin nitrogen owing to prolonged hydrolysis are probably due to carbonisation.   W. G.

Origin of the Humin Formed by the Acid Hydrolysis of Proteins. III. Hydrolysis in the Presence of Aldehydes. II. Hydrolysis in the Presence of Formaldehyde. Ross AIKEN GORTNER and GEORGE E. HOLM (*J. Amer. Chem. Soc.*, 1917, **39**, 2477—2501. Compare A., 1915, i, 726; 1916, i, 681).—The nitrogen distribution in the hydrolysates of fibrin and gelatin, obtained by boiling these proteins with hydrochloric acid and varying quantities of trioxymethylene, has been determined by Van Slyke's methods, with the modification that the humin fraction has been differentiated into (*a*) "acid-insoluble" humin, (*b*) "acid-soluble" humin, precipitated by calcium hydroxide, and (*c*) "phosphotungstate" humin, precipitated by phosphotungstic acid.

With fibrin, the addition of aldehyde increases the yield of black, insoluble humin up to a maximum, about 100% above the normal. Further quantities of aldehyde then cause a decrease in the amount of insoluble humin and an increase in the soluble humin up to a second maximum, when the continued addition of aldehyde causes decreases in the humin fractions and an increase in ammonia. With gelatin, formaldehyde has no influence on the humin fraction, which is very small, but causes a steady increase in the yield of ammonia. This difference between the two proteins is obviously to be connected with the lack of cystine, histidine, tyrosine, and tryptophan in gelatin. With which of these amino-acids the humin formation is connected can therefore be ascertained by hydrolysing mixtures of gelatin and these acids in the presence of formaldehyde. Cystine and histidine are not the critical acids. Tyrosine causes no increase in insoluble humin, but a considerable increase in soluble humin, which is not the true humin of protein hydrolysis, as it is not black but reddish-yellow. Tryptophan, however, is the all-important constituent. If this is added to gelatin, the hydrolysates correspond with those obtained from fibrin.

As tryptophan does not give rise to humin when boiled with hydrochloric acid unless an aldehyde is present, the inference is that an aldehydic substance, as yet unknown, is produced during protein hydrolysis, but not in sufficient quantity to combine with all the tryptophan, since added aldehyde gives a higher yield of humin. Indole, alone, also yields humin when boiled with hydrochloric acid and formaldehyde, so the condensation does not involve the side chain in the case of tryptophan. Pyrrole also produces humin, but not so pyridine, which suggests that whilst the pyrrole ring is critical, it is possibly not the imino-group which is connected with the condensation. That the α-amino-group of trypto-

phan remains intact in the humin is proved by the fact that the humin formed from tryptophan and trioxymethylene under the most favourable conditions contains half its nitrogen in the amino-condition, just as in the free acid. Most probably, therefore, it is position 2 of the indole complex which is concerned in humin formation.

Further experiments on mixtures of the pure amino-acids are well in hand, but the authors are already convinced that tryptophan and some aldehydic component of the protein molecule are the only factors involved, and they adversely criticise Roxas's results in the same field (A., 1916, i, 797). J. C. W.

Helicorubin. I, II. CH. DHÉRÉ and G. VEGEZZI (*J. Physiol. Path. gén.*, 1917, **17**, 44—52, 53—67. Compare A., 1917, i, 421). —The bile of the snail *Helix pomatia* contains a dialysable red pigment, helicorubin (Krukenberg, = enterohæmatin of MacMunn), and a non-dialysable, brown pigment, for which the name *helico-fuscin* is suggested by the present authors. By means of acidified alcohol, helicorubin is transformed into hæmatin, spectrometrically identical with the substance obtained from vertebrate hæmoglobin. Potassium permanganate changes helicorubin into the same pigment with absorption band in the yellow as is obtained from hæmatin, and, finally, sodium hyposulphite reduces helicohæmatin to hæmato-porphyrin (of vertebrates). The bile was obtained from hibernating snails, free from chlorophyll.

These experiments show helicorubin to be an "embryonic or ancestral" form of hæmoglobin, as was already surmised by Sorby and by MacMunn. G. B.

"Carbohydrate" Group of the True Nucleic Acids. II. R. FEULGEN (*Zeitsch. physiol. Chem.*, 1917, **100**, 241—258. Compare A., 1914, i, 1098).—The elementary analysis of sodium nucleate prepared from the thymus indicates the empirical formula

$$C_{43}H_{47}O_{25}N_{15}P_4Na_4$$
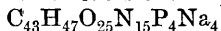
for the substance. A study of the hydrolytic products shows, however, that if the carbohydrate groups present in the molecule consist of dextrose, the molecular weight of sodium nucleate must be considerably larger than that indicated by the above formula. The author finds that, as a matter of fact, the carbohydrate groups consist of glucal (compare Fischer, A., 1914, i, 252) instead of dextrose molecules, the chief reactions of glucal being given by the carbohydrate isolated from the hydrolytic products of the nucleate. The assumption of glucal ($C_6H_{10}O_4$) instead of dextrose ($C_6H_{12}O_6$) molecules also stands in harmony with the above empirical formula. H. W. B.

The Rennetic Properties of Pepsin. HOWARD T. GRABER (*J. Ind. Eng. Chem.*, 1917, **9**, 1125—1126).—In comparative estimations of the rennetic activity of calf rennet and of pepsin from the hog's stomach, it was found that whereas the former never failed

to coagulate fresh milk or to give comparable results when diluted, the latter usually failed to coagulate fresh milk and did not show an activity proportional to its dilution. The pepsin was most active in milk of an acidity of 0·2% or more, whilst the activity of the rennin was not promoted by such high concentration of acid. By bringing the acidity of fresh milk to 0·185% by the addition of lactic acid, the results were comparable with those produced in fresh milk by the rennet. These results support the view that the two enzymic activities of pepsin are associated in a single molecule, and that on contact with milk and acid, or protein and acid, coagulation of the milk or hydrolysis of the protein is effected (see also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.).   C. A. M.

Some Nitrogenous Auxoamylases. ELBERT W. ROCKWOOD (*J. Amer. Chem. Soc.*, 1917, **39**, 2745—2752).—An examination of the effect of various nitrogenous substances on the hydrolytic activity of the amylases of the saliva on starch, those which increase the activity being called auxoamylases. a-Amino-acids, whether aliphatic or cyclic, act as auxoamylases, this being true in the case of cyclic compounds whether the amino-group is in a side chain, as in tyrosine, or in the ring, as in the aminobenzoic acids. The position of the amino-group in the benzene ring with reference to the carboxyl group has no effect on the activity. Not only do the acid amides not act as auxoamylases, but the entry of an amino-group in the carboxyl group destroys the effect of an amino-group elsewhere in the molecule. Thus aspartic acid is an auxoamylase, asparagine is not. The sulphonyl group, if substituted for the carboxyl group in an amino-acid, destroys the stimulating effect of the amino-group on the amylases. Replacement of one of the hydrogen atoms in an amino-group by an acyl group, as in hippuric acid, does not destroy its stimulating action. Imides, however, are not auxoamylases. The proteins act as auxoamylases towards ptyalin, the effect increasing as the number of free amino-groups increases by the hydrolysis of the protein. As far as the tests go, they indicate that amino-acids act as auxoamylases not only on ptyalin, but also on the pancreatic amylase.   W. G.

Supposed Action of Potassium Permanganate with Plant Peroxydases. H. H. BUNZELL and H. HASSELLRING (*Bot. Gaz.*, 1917, **63**, 225—228; from *Physiol. Abstr.*, 1917, **2**, 544). —Permanganate, reduced to a brown solution by excess of various organic substances, can still oxidise guaiacum, pyrogallol, or potassium iodide, and on the basis of these experiments the authors criticise the conclusion drawn by Reed (compare A., 1917, i, 423, 424), when he observed this phenomenon with horse-radish extract, that a specific interaction of peroxydase with permanganate was taking place to give a high-grade oxygenating substance.   G. B.

Physiological Chemistry.

The Chemistry of the Proteins. I. The Protein Fractions of Blood-plasma. II. The Theory of the Agglutination of Bacteria. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1917, **83**, 228—243).—I. The theory is put forward that the various protein fractions of the plasma, such as fibrinogen, globulin, albumins, etc., are not chemical individuals, but form a series of which the individual members can pass one into another. The more complex proteins are assumed to be liberated from the cells in a state of low aggregation, with comparatively small amounts of adsorbed simple substances to keep them in a colloidally dispersed state, from which they can be readily flocculated by salts, etc. In the course of time, the state of aggregation is finer and the amount of adsorbed substances is increased, and the proteins are not then so readily precipitated. By alteration in the state of aggregation and amount of adsorbed simpler substances, variations in the physical properties can be produced, and a blood protein can thus be varied in its properties so as to pass from a readily aggregating substance like fibrinogen through a globulin to an albumose. Experiments which are stated to substantiate this theory are quoted.

II. Bacteria are supposed to act like colloidal solutions of certain proteins, which can be precipitated by neutral salts, weak acids, etc., and are changed in their properties as regards aggregation by adsorption of various substances from sera containing anti-substances. In this respect, the theory of the authors does not differ markedly from that of others. It differs, however, in that they do not lay so much stress on the effect of electrical discharge on the flocculation as on the effect of various adsorbed simpler substances on the capacity of the bacteria for holding water. The optimal conditions for flocculation often coincide with the point of electrical discharge, because at this point the solubility of the adsorbed substances in water is smallest. 　　S. B. S.

Rate of Formation of Fibrin Ferment from Prothrombin by the Action of Thrombokinase and Calcium Chloride. JOHN MELLANBY (*J. Physiol.*, 1917, **51**, 396—403).—The formation of fibrin ferment proceeds in a manner similar to that observed in the activation of trypsinogen by enterokinase (Mellanby and Woolley, A., 1913, i, 113, 662); in both cases the velocity of the change is small at the outset, but the reaction proceeds with a constantly increasing acceleration. It is suggested hypothetically that the ultimate agent in the activation is the calcium ion, which does not act on pure prothrombin, but on prothrombin which has adsorbed thrombokinase, for the reaction is accelerated both by an increase in the calcium concentration and by an increase in the thrombokinase. 　　G. B.

Metabolism of Arginine. IV. Effect on the Secretion of Total Creatinine. W. H. Thompson (*J. Physiol.*, 1917, **51**, 347—376. Compare A., 1917, i, 673).—Whereas arginine alone, given hypodermically to dogs, is converted into creatinine only to the extent of 4·5%, the addition of methyl citrate brings about a 7% conversion. When the substances are given by the mouth, there is no increased methylation of the guanidine nucleus, or when methyl benzoate replaces methyl citrate in the hypodermic experiments. Small hypodermic doses of guanidine carbonate gave an increase in the creatinine output up to 10·8% of the guanidine injected.   G. B.

Oxydones. L. Lopez-Pérez (*Compt. rend. Soc. Biol.*, 1917, **80**, 326—327).—The oxydones of Batelli and Stern (which these authors consider responsible for the respiration of animal tissues and the oxidation of citric, fumaric, malic, and succinic acids, and of *p*-phenylenediamine) are not attacked by erepsin or by nuclease or takadiastase, so that the oxydones are not albumoses or peptones, or nucleic acid, or polysaccharides.   G. B.

Changes in the Chemistry of the Brain as a Result of Intoxications. J. E. Abelous and L. C. Soula (*J. Physiol. Path. gén.*, 1917, **17**, 157—170).—Rabbits were poisoned non-fatally by crystalloids (strychnine, cocaine, chloroform) and colloids (serum-albumin, egg-albumin, urohypotensin), and twenty to thirty-five days afterwards their brains were analysed by determining the protein nitrogen, amino-nitrogen (formol titration) protein phosphorus, lipoid phosphorus, etc. This affords a measure of the fission of proteins and lipoids in the brain; the degree of fission is considerably increased as compared with normal controls. The brain, the organ of psychical memory, also has a "chemical memory" of previous intoxications. The bearing of this on anaphylaxis is considered.   G. B.

Power of Perfumes and their Solubility in Water and in Oil. E. Louis Backman (*J. Physiol. Path. gén.*, 1917, **17**, 1—4. Compare A., 1917, i, 498).—In order that a substance may be odorous, it must be sufficiently soluble both in water and in lipoids, since the cells of the receptor organ for smell are covered with a watery fluid, whilst they themselves contain lipoid granules. Thus, the odours of the series of homologous alcohols first increase as the molecular weight rises, and then decrease again. The lower ones are comparatively odourless because little soluble in fats, cetyl alcohol because little soluble in water. Butyl alcohol, soluble in water and fats, has a powerful odour. The same applies to benzene, toluene, xylene, and ψ-cumene, and to isomeric butyl and amyl alcohols; also to the three nitrophenols and nitrotoluidines, to the dimethyltoluidines, bromoanilines, naphthylamines, etc. The changed solubility in water and in oil also explains why the introduction of an acetyl group renders alcohol odorous and aniline inodorous.   G. B.

The Imbibition of Water by Muscular Tissue, with Special Reference to the Action of Caffeine. ALEXANDER BELÁK (*Biochem. Zeitsch.*, 1917, **83**, 165—217).—The rate of imbibition of various frogs' muscles was determined. The first stage is rapid increase in the water content of the tissue, which is regarded as an osmotic phenomenon, produced by the osmotic pressure of the inner contents of the tissue. The first stage is followed by a loss of water, due to a diffusion outwards of the salts, which process is accelerated by an increase of the permeability of the membranes. The third stage of the action of water is the ordinary imbibition by colloids which follows the laws of colloidal chemistry. The action of caffeine consists apparently, in the first instance, in causing an increase in the permeability by water, followed by a transient increase in the capacity for binding water. The toxic action consists in the coagulation of the proteins, which leads to a release of water by the tissues. S. B. S.

What Substance is the Source of the Light of the Firefly ? E. N. HARVEY (*Science*, 1917, **46**, 241—243; from *Physiol. Abstr.*, 1917, **2**, 460. Compare A., 1917, i, 365—366, where in the second abstract photophlein should be photophelein).—Evidence is presented for the following conception. A colloid (photogenin) is oxidised and made to emit light under the influence of a thermostable dialysable substance (photophelein). The latter is cytolytic in its nature, and encourages oxidation by disintegrating the colloid aggregates and multiplying their surface relations. [Compare also Goss, *J. Biol. Chem.*, 1917, **31**, 271; Harvey, *ibid.*, 311.] G. B.

Saturated Hydrocarbons in Basking-shark Liver Oil. MITSUMARU TSUJIMOTO (*J. Ind. Eng. Chem.*, 1917, **9**, 1098—1099).—The liver-oil of the basking-shark, *Cetorhinus maximus*, contains 41·92 to 55·51% of unsaponifiable matter, of which the unsaturated hydrocarbon *squalene* (Tsujimoto, A., 1916, i, 786) is a constituent (compare Chapman, T., 1917, **56**, 111). On distillation under a pressure of 5 mm. of the unsaponifiable matter from one specimen of the oil, 10% of a yellow liquid distilled between 170° and 190°, whilst at 244—260°, squalene (25%) distilled. The first fraction was washed with sodium hydroxide solution, and then distilled at 160—166° under 13 mm. pressure. It was a colourless, mobile liquid, which did not solidify when cooled below 0°. It had D_4^{15} 0·8768, refractive index n_D^{20} 1·4398, and iodine value 4·4. It began to boil at about 294° under 766 mm. pressure, and distilled almost completely at 296°. Its elementary composition (C = 84·39; H = 15·02%) and molecular weight (mean, 259) corresponded most closely with the formula $C_{18}H_{38}$. Since, however, normal octadecane is solid at the ordinary temperature, this hydrocarbon is probably an *iso*octadecane, and its low boiling point may be due to this cause. The specific refraction (n^2 formula) was 0·3283, and the molecular refraction 83·4. This hydrocarbon or mixture of hydro-

carbons was not present in two other specimens of the oil (see also *J. Soc. Chem. Ind.*, 1918, **37**, Feb.).   C. A. M.

Erepsin in Normal Urine and its Relation to other Proteases. S. G. HEDIN and Y. MASAI (*Zeitsch. physiol. Chem.*, 1917, **100**, 263—303).—The urine contains an enzyme which is capable of breaking down peptone and similar protein substances in alkaline solutions. It is isolated by saturating the urine with ammonium sulphate, dissolving the precipitate in water, and then dialysing until free from sulphate. The enzyme prepared in this way from human urine can sometimes digest caseinogen and some other proteins. It is suggested that this exalted ereptic action may be due to a true erepsin or, more probably, to a mixture of erepsin with another proteolytic enzyme.

Other proteolytic enzymes are also found in normal urine, namely, enzymes which effect the degradation of serum globulin and fibrin. They act best in an alkaline medium; and the above proteins, with the co-operation of the urinary erepsin, may be completely degraded to amino-acids. The effect of the co-operative action of the proteolytic and ereptic enzymes is considerably greater than the sum of the effects produced by the two enzymes working separately. The exalted proteolysis is observed, no matter whether the co-operating erepsin has been obtained from the urine, the intestinal wall, or from yeast cells.   H. W. B.

Fat Content of Human Gall-stones. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1917, **100**, 259—262).—The specimen of human gall-stones examined was free from fat, but contained a resinous substance resembling fat in its solubility in ether and other solvents (compare A., 1917, i, 716).   H. W. B.

The Relation between Chemical Constitution and Physiological Action. FRANK LEE PYMAN (T., 1917, **111**, 1103—1128).—A lecture delivered before the Chemical Society on December 6th, 1917.   H. M. D.

Chemistry of Vegetable Physiology and Agriculture.

Effects of Oxygen and Carbon Dioxide on Nitrification and Ammonification. J. K. PLUMMER (*Cornell Univ. Agr. Expt. Stat.*, 1916, *Bull.* 384, 305—330; *Physiol. Abstr.*, 1917, **2,** 569).—Nitrification takes place in sealed flasks as long as there is a supply of oxygen; the optimum amount is 35—60%. Carbon dioxide is produced when lime is used; ammonium sulphate without lime causes only a slight increase in nitrification. If oxygen is present, carbon dioxide has no material effect. Under anaerobic

conditions, denitrification sets in, until all nitrates are destroyed. There is no optimum content of oxygen for ammonia production, but in its absence somewhat less is produced. G. B.

Influence of the Chemical Structure of the Compounds to be Ammonified on the Rate of Ammonification. K. MIYAKE (*J. Amer. Chem. Soc.*, 1917, **39**, 2378—2382).—An investigation on the relationship between the structure of organic nitrogen compounds and the rate at which they are converted into ammonia in the soil. Quantities of 100 grams of various air-dried soils were mixed respectively with 100 c.c. of water and quantities of leucine, tyrosine, acetanilide, benzanilide, acetamide, and benzamide containing 100 milligrams of nitrogen. The mixtures were allowed to incubate for periods of two, seven, twelve, and sixteen days, and the amount of ammonia formed was estimated. The rate at which the conversion into ammonia took place followed the order : acetamide > leucine > tyrosine > benzamide > acetanilide > benzanilide. It is shown that aliphatic nitrogen compounds are more rapidly converted into ammonia than aromatic compounds and aromatic amino-compounds more rapidly than aromatic imino-compounds under the conditions of the experiment. J. F. S.

Assimilation of Lactic Acid by Yeasts, and the Production of Pyruvic Acid by Yeasts and Oidia. P. MAZÉ and M. RUOT (*Compt. rend. Soc. biol.*, 1917, **80**, 336—339. Compare A., 1917, i, 310).—Yeasts grown in a confined atmosphere in a solution containing mineral salts and 2% of calcium lactate give about a 50% yield of pyruvic acid. By means of gas analyses and of the calcium carbonate formed, it is shown that the respiratory. quotient is the same as that of the controls without lactate (about 0·7), which may indicate that the yeast burned proteins and possible traces of fat; the combustion of carbohydrate reserves would give a quotient equal to 1. The culture fluids contained also a small quantity of succinic and acetic acids, but no alcohol or aldehyde. Six species of *Oidium* behaved similarly. G. B.

The Culture of Yeast in Presence of Air with the Use of Carbamide as the Source of Nitrogen, and with different sources of Carbon. The Quotient of Sugar Assimilation. TH. BOKORNY (*Biochem. Zeitsch.*, 1917, **83**, 133—164).—A detailed account is given of a large number of experiments in which the increase in dry weight is determined when yeast is grown in diluted urine to which various sugars, glycerol, etc., are added as the source of carbon. The quotient of the sugar assimilation, that is, absolute increase in dry matter/amount of sugar employed, was determined in many cases. S. B. S.

Hexose-diphosphoric Acid, its Composition and its Rôle in Alcoholic Fermentation; the Behaviour of the Sugars with Three Carbon Atoms towards Yeast. CARL NEUBERG, ADAM LEVITE, and ERWIN SCHWENK (*Biochem. Zeitsch.*, 1917, **83**, 244—268).—The authors confirm the results of Harden and Young

in ascribing to hexose-phosphoric acid the formula $C_6H_{10}O_4(PO_4H_2)_2$. Its rotation is $[\alpha]_D^{15} = +3.55°$, and it yields lævulose on hydrolysis. Neither it nor its salts can be fermented by living yeasts, even in presence of co-ferments or artificial activators, and this is not due to any toxic action on yeast cells. The esterification of phosphates takes place to the extent of only about 8% in presence of living cells even when toluene has been added, whereas the esterification of the phosphate by sugars is almost quantitative in presence of dried yeast or cell-free yeast juices. For these reasons, the formation of hexose-phosphate is regarded as a pathological process. There is no evidence, therefore, that a hexose-phosphate forms an intermediate stage in the degradation of a six-carbon into a three-carbon sugar. Neither glyceraldehyde nor dihydroxyacetone, furthermore, undergoes fermentation in the presence of yeast as does dextrose or lævulose, even in presence of activators, and this is shown not to be due to any toxic action on the yeast. Furthermore, trioses on distillation yield methylglyoxal, which can be separated in the form of its p-nitrophenylosazone, and this reaction is quantitative. On subjecting hexose-phosphoric acid prepared in different ways to this process, no triose could be detected. All evidence, therefore, is against the theories that the trioses are intermediary products of sugar fermentation and that hexose-phosphoric acids play a part in the production of such products (theory of Lebedev and others).   S. B. S.

Pharmacological Studies of the Ipecacuanha Alkaloids and some Synthetic Derivatives of Cephaeline. III. Protozoöcidal and Bactericidal Action.

A. L. WALTERS, W. F. BAKER, and E. W. KOCH (*J. Pharm. Expt. Ther.*, 1917, **10**, 341—364. Compare Walters, Eckler, and Koch, A., 1917, i, 717). —When solutions of emetine hydrochloride of 0·0005% strength are in contact with cultures of amœbas for an hour, many of the amœbas are destroyed, but transplants from these cultures to fresh agar plates show a certain amount of growth of amœbas which is retarded or delayed, due probably to the development of encysted or resistant forms. Stronger solutions of emetine hydrochloride are more toxic, but even when a 1% solution is employed, some amœbas may still be living at the end of an hour. The propyl and *iso*amyl ethers of cephaeline are more toxic towards amœbas than emetine.

Methylating cephaeline to form emetine is known to increase the toxic action towards *Endamœba buccalis* and paramœcia, and the substitution of the methyl group by ethyl, propyl, butyl, *iso*amyl, or allyl further intensifies this action. Cephaeline *iso*amyl ether phosphate is the most effective alkaloid of this group in killing paramœcia, being fifteen to twenty times as potent as emetine phosphate.

Tested on *Staphylococcus aureus* in the manner described, cephaeline propyl ether phosphate is bactericidal in solutions of 0·5% strength, and the corresponding *iso*amyl ether in solutions of

0·025% strength. Both these derivatives are much stronger than emetine in bactericidal action. H. W. B.

The Disinfectant Action of Quinine Derivatives on Diphtheria Bacilli. HANS SCHAEFFER (*Biochem. Zeitsch.*, 1917, **83**, 269—314).—Quinine shows an inhibitory action towards diphtheria bacilli in a concentration of 1 : 10,000. This action is not greater in the cases of hydrocupreine and its methyl, ethyl, and *iso*propyl derivatives. *iso*Butylcupreine is, however, more active, being antiseptic in a concentration of 1 : 50,000. *iso*Amyl, hexyl, heptyl, and octyl derivatives show increased antiseptic activity with increasing molecular weight, the octyl derivative being active in the concentration 1 : 750,000. The decyl derivative is less active (1 : 500,000), and from this substance onwards the activity of the derivatives progressively diminishes with increasing molecular weight until the cetyl derivative is active only in a concentration of 1 : 5000. The lethal action of the disinfectants runs for the most part parallel with their inhibitory action; an exception was found in the case of hexylhydrocupreine, which has a greater antiseptic action than its next lower homologue (*iso*amylhydrocupreine), but a smaller disinfecting action. The monhydrochlorides of the alkaloid were more active than the dihydrochlorides. The hydrocupreine derivatives showed good disinfecting action in human serum. S. B. S.

Behaviour of some Organic Substances in Plants. IX. G. CIAMICIAN and C. RAVENNA (*Gazzetta*, 1917, **47**, ii, 109—130. Compare A., 1917, i, 681).—The experiments described in the first part of this paper were carried out by watering germinating seeds or plants with dilute solutions (0·1%) of various organic substances. Mandelonitrile almost prevents germination, but when it is administered to seedlings, their growth is not prevented, although the mature plants have a habit of growth so abnormal as to give the appearance of a new species. In such plants hydrogen cyanide and benzaldehyde could not be detected either before or after the addition of emulsin. Normal adult plants are killed if mandelonitrile is administered to them.

Amygdalin does not prevent germination. Strychnine does not prevent germination, but has poisonous effects afterwards. Nicotine hinders germination and affects growing plants adversely. Morphine and caffeine resemble strychnine in their action.

In the second part of the paper experiments are described dealing with the action of triturated spinach on solutions of various organic substances, toluene being added to prevent putrefaction, and a slow current of oxygen being passed to assist any oxidative processes. The escaping gas is passed through barium hydroxide solution and the precipitated barium carbonate is weighed. In these conditions, catechol and saligenin are acted on to a considerable extent, tartaric acid and salicylic acid to a lesser extent, whilst benzoic acid, pyridine, piperidine, and nicotine remain unaltered.

R. V. S.

Permeability. V. The Swelling of Plant Tissue in Water and its Relation to Temperature and Various Dissolved Substances. WALTER STILES and INGVAR JØRGENSEN (*Ann. Bot.*, 1917, **31**, 415—434).—Experiments with uniform disks of potatoes and carrots show that these vegetables, when immersed in distilled water, absorb water (swell) for some days before equilibrium is attained, and then it is maintained for several days. The rate of swelling of carrot is much greater than that of potato, the amount of swelling being influenced by the previous history of the tissue. In tap water the swelling is less than in distilled water, and equilibrium is not maintained for so long, a shrinkage of the tissue ultimately occurring. Rise of temperature causes an increase in the rate of swelling. In solutions of sodium chloride or sucrose, the swelling of potato or carrot diminishes with increase in the concentration of the solution, and may become a shrinkage. For the potato the approximate concentrations of isotonic solutions are $N/8$-sodium chloride and $M/4$-sucrose, and for the carrot $N/3$-sodium chloride. With the primary alcohols, preliminary swelling takes place in solutions of much higher concentration than isotonic solutions, and is followed by shrinkage in all concentrations. This shrinkage is due to toxic action and not to plasmolysis. Acids behave in a manner similar to the primary alcohols. W. G.

Tuba, an East Indian Poison for Fish. T. ISHIKAWA (*Tokyo Igakkwai Zasshi*, 1916, **30**, 45—46; *Jap. Med. Lit.*, 1917, **1**, 7—8; from *Chem. Abstr.*, 1917, **11**, 2371).—Tuba is the Malay name for the plant *Derris elliptica*, Benth., and is used to kill fish. *Tubatoxin*, $C_{18}H_{18}O_5$, forms white crystals from alcohol, m. p. $163.5°$, soluble in most organic solvents, but not in water or in acids and alkalis; it reduces ammoniacal silver and alkaline copper solutions; a sensitive colour test is described. Tubatoxin produces in fish, frogs, and mammals general motor paralysis. The lethal dose for a rabbit (intravenous) is 0.0009 gram per kilo. Compare also Greshoff, A., 1891, 335; van Sillevoldt, A., 1900, i, 109; Power, A., 1903, ii, 323. G. B.

Chemical Constituents of Uzara Root. W. HENNIG (*Arch. Pharm.*, 1917, **255**, 382—405).—Uzara root, the valuable anti-diarrhœtic properties of which have been described by Gürber (*Münch. med. Woch.*, 1911, No. 40), appears to be identical with Warsicky's ithongua (*Ber. deut. Pharm. Ges.*, 1916, **26**, 266).

The dried, alcoholic extract of the root, which is known as uzaron, has been examined, and only one of the three crystalline substances mentioned by Gürber (*loc. cit.*) has been obtained. Uzaron is shaken with hot water (4 parts), the clear, aqueous solution, when cold, is separated from the upper layer of fatty and resinous substances, treated with freshly prepared 20% tannin solution so long as a precipitate is obtained (an excess is to be avoided), the mixture is stirred for twenty-four hours, the brown, plastic mass which has separated is collected, kneaded in a current of water, made into

a viscous broth with zinc oxide and water, and evaporated to dryness. The residual mass is finely powdered, extracted with methyl alcohol in a Haussmann vacuum distillation apparatus, the excess of alcohol is distilled from the extract, and the residue, which after being dried over sulphuric acid in a desiccator represents about 50% of the uzaron, is shaken for many hours with cold water; the insoluble portion is finally purified by repeated crystallisation from 50% alcohol and from hot water. The product is a glucoside, uzarin, the yield being about 10% of the uzaron or about 2·5% of the uzara root. *Uzarin*, $C_{75}H_{108}O_{80},9H_2O$, slender, colourless needles, m. p. about 210°, decomp. about 200°, is sparingly soluble in aqueous sodium hydroxide and in the usual solvents at the ordinary temperature, but dissolves comparatively easily in hot water. The solution has a neutral reaction, gives a precipitate with tannic acid, but not with neutral or basic lead acetate, and exerts a slight reducing action on bismuth nitrate, Fehling's soluiton, and ammoniacal silver nitrate after prolonged boiling. The colour reactions of uzarin are described. The glucoside does not contain methoxyl groups. It is easily hydrolysed by hot 2% sulphuric acid, yielding 1 mol. of propyl alcohol (identified in the form of barium propionate) and 3 mols. each of dextrose and uzaridin, a portion of the latter being obtained as anhydrouzaridin (see below). *Uzaridin*, $C_{18}H_{24}O_5$, forms colourless leaflets containing $\frac{1}{2}H_2O$, and when anhydrous has decomp. about 246°. It is insoluble in water, but dissolves in hot dilute alcohol, the solution having an intensely bitter taste. The *triacetyl* derivative, prepared by boiling with acetic anhydride, forms large, colourless needles, m. p. 225—227°, and when it is hydrolysed by boiling alcoholic $N/2$-potassium hydroxide, the amount of alkali neutralised is more than that corresponding with three acetyl groups. Under the same treatment, uzaridin itself is found to neutralise potassium hydroxide, although in what way cannot at present be stated.

Anhydrouzaridin, $C_{18}H_{22}O_4$, forms colourless needles containing $\frac{1}{2}H_2O$, and when anhydrous has decomp. 208—214°.

The alcoholic mother liquors obtained during the purification of urazin contain a small amount of a second glucoside, which is amorphous and differs from uzarin in its physiological action and in its extremely bitter taste.   C. S.

Toxicity of Galactose and Mannose for Green Plants and the Antagonistic Action of other Sugars towards these. L. KNUDSEN (*Amer. J. Bot.*, 1917, **4**, 430—437; from *Physiol. Abstr.*, 1917, **2**, 561).—Plants were grown in culture tubes on agar with a modified Pfeffer's salt solution under conditions excluding micro-organisms. Galactose and mannose in 0·025 molar solutions were very toxic to the roots of peas and wheat. Dextrose and sucrose act as antidotes.   G. B.

Organic Plant Poisons. I. Hydrocyanic Acid. WINIFRED E. BRENCHLEY (*Ann. Bot.*, 1917, **31**, 447—456).—Hydrocyanic acid

is very toxic to peas and barley.   Down to a dilution of 1 in
100,000, peas are killed either immediately or after a short interval
of poor growth.   In the case of barley, strong concentrations kill
the plant, but at the above dilution there is a period during which
no growth occurs, after which there is slight progress, but no normal
growth.   Sodium cyanide is just as toxic as hydrocyanic acid, but
formic acid, except in very high concentrations, is comparatively
harmless to barley.   In no case was there any indication of stimu-
lation in peas or barley, even at very great dilutions, with any of
the compounds tested.

Pea plants killed by hydrocyanic acid shrivel from the cotyledons
upwards, and the roots contract intensely.   Barley roots will not
enter strong solutions, but often put out laterals which stop short
at the surface of the solution.   W. G.

Effect of Sulphur on Different Crops and Soils.   O. M.
SHEDD (*J. Agric. Research*, 1917, **11**, 91—103).—Soja beans, clover,
oats, lucerne, and wheat were grown in pots on eight different
types of soil, which received applications of flowers of sulphur at
the rates of 100 lb. and 200 lb. per acre, together with calcium
carbonate and other fertilisers as applied to the controls.   It was
found that the sulphur increased the production of some crops, had
no effect on others, and on some was injurious, the results depending
on the crop and soil.   On the whole, there was a majority of small
increases.   The sulphur increased the total sulphur and sulphate-
sulphur of the crop.   In the cases of clover and lucerne, the excess
sulphur in the plants was in the form of sulphate, but in soja beans
part of the excess was in another form, not necessarily protein, since
an increased protein content was not always found with an increased
sulphur content.

Germination tests with sixteen varieties of seeds showed that all
except two formed a greater or less amount of sulphate on germin-
ating, the increase varying from 0·0 to 0·035% on the weight of
seed.   W. G.

Nitrogen, Chlorine, and Sulphates in Rain and Snow.
E. LYLE PECK (*Chem. News*, 1917, **116**, 283—284).—A continua-
tion of the work of Artis (compare A., 1916, i, 304).   Forty-one
samples of rain and snow were examined between October, 1916,
and June, 1917.   The following results, expressed as parts per
million, were obtained: sulphate, 4·3—36·39; nitrate, 0·10—0·50;
nitrite, 0·0005—0·208; nitrogen in free ammonia, 0·097—0·872;
nitrogen in albuminoid ammonia, 0·057—0·68; chlorine, 2·84—18·62.
The chlorine was most constant, being 7·1 parts per million in
twenty of the samples.   The total fall during the period amounted
to 15·86 in. of rain and 22 in. of snow.   W. G.

Organic Chemistry.

A System of Organic Nomenclature. AUSTIN M. PATTERSON and CARLETON E. CURRAN (*J. Amer. Chem. Soc.*, 1917, **39**, 1623—1638).—An account, with examples, of the principles observed by the authors in their work of indexing organic compounds for the forthcoming Decennial Index of *Chemical Abstracts*.

J. C. W.

Solubility of Iodoform in Glycerol. CHIARIA (*Giorn. Farm. Chim.*, 1917, **66**, 94—96; from *Chem. Zentr.*, 1917, ii, 483).—The solubility of iodoform in glycerol (D^{15} 1·256) is 0·123%.

R. V. S.

The Cause of the Anomalies shown in the Dissociation of Amylene Hydrobromide and its Consequences. ALB. COLSON (*Compt. rend.*, 1918, **166**, 71—73).—The irregularities occurring in the dissociation of amylene hydrobromide, b. p. 107°, when heated for a long time at 184° under different pressures (compare Lemoine, A., 1891, 970), are shown to be due to the partial conversion of this hydrobromide, $CMe_2Br \cdot CH_2Me$, into its isomeride, $CHMe_2 \cdot CHMeBr$, b. p. 124°. W. G.

An Alcohol Receipt of the Eighth Century. H. DEGERING (*Sitzungsber. K. Akad. Wiss. Berlin*, 1917, 503—515; from *Chem. Zentr.*, 1917, ii, 366—367).—A manuscript of the twelfth century lately received by the Royal Library in Berlin gives a recipe for the preparation of "*aqua ardens*" which agrees with another made known by Puccinotti from a manuscript at San Gimignano. Both texts are probably derived from an original belonging to the eighth century. The process described must have yielded at least 35 vol. %, for the sulphur test is described, and burning sulphur cannot be extinguished with a more watery liquid. R. V. S.

The Action of Phosphoryl Chloride on Methyl or Ethyl Alcohol. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1917, **101**, 225—228. Compare A., 1917, i, 625).—Experiments have now been made to determine what by-products are formed during this reaction. If excess of ethyl alcohol is used, and the reaction mixture distilled at 215—220°, a small quantity of distillate (3—5% of the weight of the mixture) is obtained containing normal pyro- and ortho-esters. By neutralising the product from the action of excess of alcohol on phosphoryl chloride with barium hydroxide, using phenolphthalein as indicator, from 50—70% of the product is obtained as the salt, $BaC_2H_5PO_4$. It is shown experimentally that the tri-ester, Et_3PO_4, is decomposed at 100° by dry hydrogen chloride, with formation of the mono-ester, according to the equa-

tion $Et_3PO_4 + 2HCl = 2EtCl + EtH_2PO_4$, and it is suggested that the hydrochloric acid formed by the interaction of alcohol and phosphoryl chloride may have an important influence on the final products. The experiments fail to determine whether ortho-esters are produced by the replacement of the third chlorine atom in the phosphoryl chloride molecule by the alcohol radicle, or synthetically from the meta-ester and alcohol according to the equation $3EtPO_3 + 3EtOH = Et_3PO_4 + EtH_2PO_4 + Et_2HPO_4$.

The reaction is complicated by the presence of different solvents. For instance, in presence of ether, practically no ethyl chloride is formed.   E. H. R.

[**Preparation of**] **Paraffin Ethers.** THE. ROESSLER AND HASSLACHER CHEMICAL CO., NEW YORK (U.S. Pat., 1245742, 1917; from *J. Soc. Chem. Ind.*, 1918, 20A).—A vaporised mixture of a chlorine derivative of a hydrocarbon with an inert gas is passed over a basic oxide, such as lime, at 250—450°; thus, for the preparation of ethyl ether, a mixture of chlorine (1 vol.) with ethane (3 vols.) is caused to react at 300—550°, and, after the removal of hydrogen chloride, the mixture of ethyl chloride and ethane is dried and then submitted to the action of lime.   D. F. T.

Action of [Sodium] Arsenite and [Mixtures of Potassium] Sulphide and Cyanide on Hypochlorous Esters. A. GUTMANN (*Ber.*, 1917, **50**, 1717—1718).—Ethyl hypochlorite reacts with sodium arsenite solution to form normal sodium arsenate and ethyl alcohol, and with a mixture of potassium cyanide and hydrosulphide according to the equation $EtOCl + KCN + KSH = KCNS + KCl + EtOH$.   J. C. W.

Lecithin. I. "Hydrolecithin" and its Bearing on the Constitution of Kephalin. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1918, **33**, 111—117).—Hydrolecithin is readily produced by the reduction of lecithin with hydrogen in the presence of palladium. After recrystallisation from methyl ethyl ketone, it softens, on heating, between 80° and 90°, turns brown about 100°, starts to melt about 200°, and runs down the tube, giving a dark red liquid, at 235°. According to Paal and Oehme (A., 1913, i, 584), it sinters at 83—84° and decomposes above 150°. The optical rotation is $[\alpha]_D^{20} + 5\cdot3°$. As thus prepared, the hydrolecithin is not pure, but contains 20% of a substance containing amino-nitrogen, which, from a consideration of the results of the elementary analysis and the isolation after hydrolysis of the auri-chloride of aminoethyl alcohol, the authors believe to be hydro-kephalin. [See also *J. Soc. Chem. Ind.*, 1918, 136A.]   H. W. B.

Drying Oils. I. The Properties of some Cerium Salts obtained from Drying Oils. ROBERT SELBY MORRELL (T., 1918, **113**, 111—124).—Cerous salts of the normal type, CeX_3, have been prepared from palmitic, stearic, oleic, elaidic, linoleic, α- and β-elæostearic, linolenic, and abietic acids. When

freshly prepared, the oleate, linoleate, linolenate, a-elæostearate, and abietate are soluble in ether or turpentine, but the other salts are insoluble. The ethereal solutions of the salts of the unsaturated acids darken on exposure to air, the linolenate reacting according to the equation $4CeX_3 + 3O_2 = 2CeO(XO_2)_2$ (a buff precipitate) $+ 2CeX_4$ (soluble). Normal salts may also be obtained from raw oils (olive, poppy-seed, linseed), but after thickening by the author's heat treatment (A., 1915, i, 75) and removing polymerides, if any, by means of acetone, the oils give insoluble basic salts of the type $CeOX_2$, and also soluble ceric salts, CeX_4.

Cerous a-elæostearate absorbs oxygen at a rate which is easily measured, giving a basic salt of the formula $Ce_2O(XO_2)_6$. The corresponding acid has peroxidic properties and gradually sets, through polymerisation, to a varnish. This oxidation of the a-elæostearate shows that the function of the salt as a drier can be represented by the scheme $CeX_3 \longrightarrow Ce_2O(XO_2)_6$, and this $+$ a drying oil $\longrightarrow CeX_3 +$ peroxidised oil. It is probable, in the light of the results now presented, that oxidation to peroxidic acids precedes polymerisation in the "drying" of oils. As the polymerisation may be catalysed by other agents than the oxidation, this would account for the common practice in the trade of using two different driers.

For experimental details, and for discussions of other problems connected with the drying of oils, see the original. J. C. W.

Resolution of the Diamminodinitro oxalatocobalt Complex and Determination of the Configurations of this Complex, and of the Tetranitrodiamminocobalt Complex. YUJI SHIBATA and TOSHIO MARUKI (*J. Coll. Sci. Tokyo*, 1917, **41**, [2], 1—12).—In a previous paper (Shibata, A., 1916, i, 277), it has been shown that the two nitro-groups in the dinitrodiamminooxalatocobalt complex, $[Co(NH_3)_2(NO_2)_2C_2O_4]M$, are in the *cis*-position with respect to each other. If the relative positions of the two ammonia molecules can now be determined, the whole configuration of the molecule is elucidated, the oxalato-residue necessarily occupying the *cis*-position. Two space formulæ are possible for this configuration, namely,
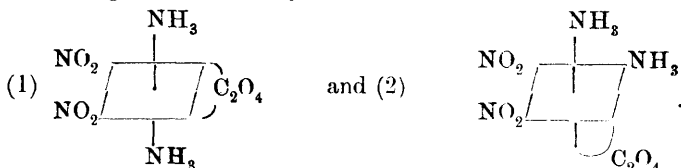
Of these two formulæ, (2) represents a compound which should be capable of being resolved into optical isomerides, so that the desired determination of the configuration should be possible. Experiments with barium dinitrodiammino-oxalatocobaltiate showed that it could readily be resolved in the usual way by means of brucine, strychnine, or cinchonine, the alkaloid salt of the com-

plex being prepared from the sulphate of the alkaloid and then fractionally crystallised. The potassium and ammonium salts of the active complex could then be obtained by the action of potassium or ammonium iodide.

The asymmetry of the complex in question is not due to the asymmetry of the cobalt atom, but to a molecular asymmetry, which is different from Werner's types I and II; it is therefore called type III of molecular asymmetry.

Since the dinitrodiammino-oxalatocobalt compound is readily obtained from the tetranitrodiamminocobalt compound by the action of oxalic acid, it follows that the two ammonia groups in the latter compound are in the *cis*-position.

The least soluble fraction of the *brucine* salt,
$$[Co(NH_3)_2(NO_2)_2C_2O_4]H, C_{23}H_{26}O_4N_2, H_2O,$$
crystallised in brown needles, aggregating in radial form, and had $[a]_D^{27\cdot5} -70\cdot7°$; its solution in water was not stable, the free alkaloid gradually being deposited. The most soluble fraction gave crystals having $[a]_D^{28} + 68\cdot3°$. The *potassium* salts,
$$[Co(NH_3)_2(NO_2)_2C_2O_4]K, 1\tfrac{1}{2}H_2O,$$
obtained from the respective brucine salts, gave $[a]_D^{27} \pm 115°$.

The least soluble *strychnine* salt,
$$[Co(NH_3)_2(NO_2)_2C_2O_4]H, C_{21}H_{22}O_2N_2, H_2O,$$
gave a potassium salt having $[a]_D^{27} -104°$, but the strychnine salt could not be prepared pure, owing to its instability. The *dextro*-potassium salt could not be obtained from the strychnine salt.

With cinchonine, the least soluble fraction separated as pale brown needles, having the formula
$$[Co(NH_3)_2(NO_2)_2C_2O_4]H, C_{19}H_{22}ON_2,$$
and $[a]_D^{27} + 149°$; the potassium salt derived from it had $[a]_D^{17} + 111°$. The more soluble fraction could not be isolated.

Ammonium salts were similarly obtained, having $[a]_D^{27} -107°$ and $+116°$ respectively.   T. S. P.

Method of Producing Acetaldehyde. E. F. SCHELLER (U.S. Pats., 1244901 and 1244902, 1917; from *J. Soc. Chem. Ind.*, 1918, 20A).—Purified acetylene mixed with steam is passed over a heated catalyst consisting of oxides or combinations of oxides; the exhausted or poisoned catalyst, for example, molybdic acid, may be regenerated by heating in a current of gas containing oxygen, for example, air.   D. F. T.

The Method of Oxidation and the Oxidation Products of *l*-Arabinose and *l*-Xylose in Alkaline Solutions with Air and with Cupric Hydroxide. J. U. NEF, OSCAR F. HEDENBURG, and J. W. E. GLATTFELD (*J. Amer. Chem. Soc.*, 1917, **39**, 1638—1652. Compare A., 1914, i, 490).—An account, with full experimental details, of the identification of the products formed by the oxidation of *l*-arabinose and *l*-xylose in alkaline solutions.

Formic acid, calcium glycollate, *l*-erythrono-γ-lactone, *d*-threono-phenylhydrazide, quinine *l*-glycerate, and calcium *d*-glycerate were actually obtained from *l*-arabinose after oxidation with air, and

glycollic acid, oxalic acid, and *l*-arabono-γ-lactone after oxidation with cupric hydroxide. *l*-Xylose gave formic acid, *l*-threono-phenylhydrazide, *d*-erythrono-γ-lactone, calcium glycollate, and calcium *l*-glycerate when oxidised by air, and *l*-xylono-γ-lactone, *d*-xylono-γ-lactone, glycollic acid, and oxalic acid when heated with alkaline cupric hydroxide. J. C. W.

The Auto-oxidation of Sugars. L. BERCZELLER and E. SZEGÖ (*Biochem. Zeitsch.*, 1917, **84**, 1—36).—Sugar in alkaline solution was shaken in the presence of air, and the influence of various substances added to the solution on the rate of oxidation was ascertained. The oxidation was measured by determining the diminution of pressure in the reaction flask after varying intervals. Some substances, such as methylene-blue, promote oxidation. The influence of tartrate and other substances on the oxidation of sugar in alkaline copper solutions was investigated. Charcoal was found to promote oxidation. S. B. S.

Lactose. A. SMITS and J. GILLIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 520—532. Compare Hudson, A., 1908, i, 952; ii, 665).—The α-anhydrous form of lactose is metastable not only below 93°, but also up to its m. p., 222·8°. The hydrate when heated at 125° in the dry condition gives the α-anhydrous form, but in the presence of its saturated solution at the same temperature always gives the β-form. The authors consider that lactose hydrate is the hydrate of the α-form, and that consequently its dehydration is accompanied by a transition of the α- into the β-anhydrous form, the transformation temperature, 93·5°, being really a transformation-dehydration point. As a consequence of this, the system water–lactose must be considered as a pseudo-ternary system, for which the authors have derived the isotherm diagram. [See also *J. Soc. Chem. Ind.*, 1918, 133A.] W. G.

Influence of different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. II. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 382—391. Compare A., 1917, i, 195, 631).—An extension of the study to the influence of α-aminobutyric acid, valine, leucine, asparagine, glutamic acid, and tyrosine. The results in every case agree with those obtained from the amino-acids previously studied.

Aniline and pyridine have no influence on the action of sodium hydroxide on dextrose, but they retard the inversion of sucrose by hydrochloric acid. [See also *J. Soc. Chem. Ind.*, 1918, 133A.] W. G.

Adsorption Compounds and Adsorption. I. The Starch–Iodine Complex. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 106—117).—It is shown that the presence of potassium iodide is not necessary for the formation of the complex. The imbibition temperature of the starch iodine complex is about 1° above that

of pure starch. Starch takes up more iodine at a lower than at a higher temperature. A secondary adsorption of iodine by starch can be demonstrated. Adsorption equilibrium between starch and iodine takes place more rapidly in dilute than in concentrated solutions.   S. B. S.

Action of Methylene Iodide on Des-dimethylPiperidine (ε-Dimethylamino-Δᵅ-pentene).

AMAND VALEUR and EMILE LUCE (*Compt. rend.*, 1918, **166**, 163—164).—Methylene iodide does not cause cyclisation when it acts on ε-dimethylamino-Δᵅ-pentene, but the compound, $C_8H_{17}NI_2$, obtained (compare Ladenberg, A., 1882, 534) is shown to be *methylene-des-dimethylpiperidine iodide* [*dimethyliodomethyl-Δ⁶-pentenylammonium iodide*],

$$CH_2\text{:}CH\cdot[CH_2]_3\cdot NMe_2I\cdot CH_2I,$$
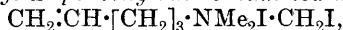
m. p. 163°, which when boiled with hydriodic acid in the presence of phosphorus gives *dimethyliodomethyl-δ-iodopentylammonium iodide*, $CH_3\cdot CHI\cdot[CH_2]_3\cdot NMe_2I\cdot CH_2I$, m. p. 136·5—137·5°. This compound with moist silver oxide gives a quaternary ammonium hydroxide which on treatment with potassium iodide yields a *compound*, $C_8H_{17}NI_2$, m. p. 143—144°, isomeric with the one described above.   W. G.

The Free Affinity of the Copper Salts of the Imino-acids.

J. V. DUBSKY and M. SPRITZMANN (*J. pr. Chem.*, 1917, [ii], **96**, 112—122).—The copper salt of iminodiacetic acid (Heintz, *Annalen*, 1862, **124**, 297; 1870, **156**, 51) in aqueous ammonia gives a deep blue solution which on evaporation deposits violet-blue needles of an additive compound of the composition $C_4H_8O_4N_2Cu,3H_2O$; in view of the composition of the corresponding compound derived from nitrosoiminodiacetic acid (see below), the constitution is probably

$$NH\underset{CH_2\cdot CO_2}{\overset{CH_2\cdot CO_2}{\diagdown\diagup}}Cu\ldots.NH_3.$$

In a similar manner, the bluish-green, microcrystalline *copper* salt, $C_4H_4O_5N_2Cu,2\frac{1}{2}H_2O$, of nitrosoiminodiacetic acid yields a violet-blue ammonia *additive* compound of the probable constitution

$$NO\cdot N\underset{CH_2\cdot CO_2}{\overset{CH_2\cdot CO_2}{\diagdown\diagup}}Cu\underset{NH_3}{\overset{NH_3}{\diagdown\diagup}},2H_2O,$$

and the green *copper* salt of nitroiminodiacetic acid forms a violet-blue *additive* compound, to which is ascribed the formula

$$NO_2\cdot N\underset{CH_2\cdot CO_2}{\overset{CH_2\cdot CO_2}{\diagdown\diagup}}Cu\underset{NH_3}{\overset{NH_3}{\diagdown\diagup}},H_2O.$$

The *copper* salt, $C_{10}H_9O_4NCu,H_2O$ (green needles), of phenylimino-diacetic acid, and the copper salts of iminodipropionic and nitro-iminodipropionic acids with ammonia form respectively the *compounds* $C_{10}H_9O_4NCu,NH_3$ (bluish-green needles and prisms), $C_6H_{12}O_4N_2Cu,1\frac{1}{2}H_2O$ (pale blue crystals), and $C_6H_{14}O_6N_4Cu,2H_2O$ (violet-blue). In all these ammonia derivatives the copper atom is regarded as assuming a maximum valency of four. With the salts of nitrilotriacetic acid, $N(CH_2\cdot CO_2H)_3$, the behaviour was less regular; the bluish-green normal *copper* salt, $C_{13}H_{12}O_{12}N_2Cu_3,7H_2O$,

yielded pale blue crystals of a violet-blue ammonia compound, $C_{12}H_{27}O_{12}N_7Cu_3,4H_2O$, whereas the pale blue acid *copper* salt, $C_6H_7O_6NCu$, gave no definite product with ammonia.   D. F. T.

Salt Formation with Nitroso-, Nitro-, and Phenylimino-diacetic Acids. J. V. DUBSKY and M. SPRITZMANN (*J. pr. Chem.*, 1917, [ii], **96**, 105—111).—Nitrosoiminodiacetic acid,

$$NO \cdot N(CH_2 \cdot CO_2H)_2,$$
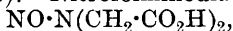
is conveniently prepared by the action of nitrous fumes on an aqueous suspension of iminodiacetic acid; the nitroso-acid is dibasic and forms an *ammonium* salt, a colourless, microcrystalline powder with $\frac{1}{2}H_2O$, and a colourless, crystalline *zinc* salt with $2H_2O$. Nitroiminodiacetic acid, $NO_2 \cdot N(CH_2 \cdot CO_2H)_2$ (Franchimont and Dubsky, A., 1916, i, 467), which is also dibasic, was converted through its *ammonium* salt, colourless leaflets with $1H_2O$, into the colourless *silver* salt, *barium* salt, crystalline mass with $2H_2O$, and *zinc* salt, an explosive, crystalline mass. Phenyliminodiacetic acid in aqueous solution reacts with silver nitrate, giving a *silver* salt, $C_{10}H_{10}O_4NAg$, needles, but the interaction of the diammonium salt with silver nitrate yields a *disilver* salt, $C_{10}H_9O_4NAg_2$, the precipitate, which is white at first, rapidly becoming yellow; the *zinc* salt, $C_{10}H_9O_4NZn,3H_2O$, was also prepared from the ammonium salt by double decomposition with zinc sulphate. With these acids, no double salts were observed of the type yielded by iminodiacetic and iminodipropionic acids.

D. F. T.

Constitution of Carbamides. V. Mechanism of the Decomposition of Urea when Heated in Solution with Alkalis and with Acids respectively. The Hydrolysis of Metallic Cyanates. EMIL ALPHONSE WERNER (T., 1918, **113**, 84—99. Compare T., 1913, **103**, 1013).—If a solution of urea in aqueous barium hydroxide is heated, ammonia can be detected in the vapour as soon as the boiling point is reached, but some minutes elapse before any barium carbonate appears. It follows, therefore, that the equation $CH_4ON_2 + Ba(OH)_2 = BaCO_3 + 2NH_3$ does not represent the facts, and that urea is not hydrolysed in this sense. The decomposition of urea by hydrolytic agents is more correctly represented in two stages: first, the dissociation of urea, which is the ammonium salt of ketonic cyanic acid, into ammonia and cyanic acid, and, secondly, the hydrolysis of the cyanic acid or alkali cyanate. Under comparable conditions, the rate at which urea is decomposed is greater in the presence of sodium hydroxide than in the presence of hydrochloric acid, because the proportion of free urea is greater in alkaline solutions than in acid, and only free urea suffers decomposition. Thus, in N-solutions, 55% of urea hydrochloride is dissociated into its components,

$$NH\text{:}C(OH) \cdot NH_2, HCl \longrightarrow NH\text{:}C{<}^{NH_3}_{O} + HCl,$$
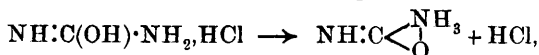
whilst the acidic property of urea is so slight that a salt of the

formula $NH:C(ONa)\cdot NH_2$ would only exist in solutions containing much urea and much alkali.

The dissociation of urea into ammonia and cyanic acid does not take place in sterile solutions, either acid or alkaline, to any appreciable extent below 90°. Thus, the velocity of the decomposition of urea at 98·2°, 71·25°, and 61·05° respectively is as 83·6 : 2·77 : 0·715. This can be verified by testing the solution from time to time with silver nitrate or barium hydroxide. The enzyme, urease, which brings about speedy decomposition at ordinary temperatures, apparently promotes direct hydrolysis of undissociated urea, for it has no influence on potassium cyanate.

The well-known fact that alcohol retards the decomposition of urea in solution, but accelerates the transformation of ammonium cyanate into urea, can only be explained satisfactorily in the light of these dissociation theories. In the first case, alcohol really retards the hydrolysis of the cyanic acid formed by dissociation of the urea, and in the second it promotes the dissociation of ammonium cyanate into ammonia and enolic cyanic acid, but does not interfere with the tautomerisation of the acid and its reunion in the ketonic form with ammonia to give urea.

The formation of urea from other cyanates than ammonium cyanate can be explained in a similar manner. Thus, the hydrolysis of potassium cyanate at ordinary temperatures is indicated by the equations: (1) $KOCN + H_2O \rightleftharpoons KOH + (HO\cdot CN \rightleftharpoons HN:CO)$, (2) $HO\cdot CN + H_2O = NH_3 + CO_2$, (3) $CO_2 + KOH = KHCO_3$, (4) $HN:CO + NH_3 = HN:C<^{NH_3}_O$, and $HO\cdot CN + NH_3 = NH_4O\cdot CN$. At higher temperatures than 80°, no ammonium cyanate would be formed.

For experimental details, see the original.   J. C. W.

Preparation of Cyanamide. A. E. OSTERBERG and E. C. KENDALL (*J. Biol. Chem.*, 1917, **32**, 297—298).—Calcium cyanamide is mixed with water, and carbon dioxide passed in until a neutral or only slightly alkaline reaction is reached. The temperature must be maintained below 40°. In these circumstances, the calcium cyanamide is quantitatively decomposed; and, after filtering off the precipitated calcium carbonate, the cyanamide is recovered from the filtrate by concentrating in a vacuum and subsequently extracting with ether. In this way, 55 grams of pure crystallised cyanamide are obtained from 200 grams of the calcium salt, corresponding with a yield of 92% of the theoretical. [Compare *J. Soc. Chem. Ind.*, 1918, **37**, 107A.]   H. W. B.

Cyanuric Acid as an Oxidation Product of Uric Acid. Its probable Identity with Tetracarbimide. C. S. VENABLE and F. J. MOORE (*J. Amer. Chem. Soc.*, 1917, **39**, 1750—1755).— Under the conditions described by Scholtz (A., 1902, i, 140), uric acid may be oxidised to cyanuric acid. With slight modifications, the yield of this product may be nearly 50% of the theoretical amount. The cyanuric acid prepared by this method has been

thoroughly identified, and it is more than likely that Scholtz was wrong in regarding his product as tetracarbimide.　　J. C. W.

New Preparation of Aliphatic Nitriles by Catalysis. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 121—123).— Aluminium oxide can be used as a catalyst in place of thorium oxide for the preparation of nitriles from the esters of cyclic acids by the action of ammonia (compare this vol., i, 68), only in this case the gas evolved consists of ethylene and hydrogen in the proportion of 2:1 if ethyl esters are used. The reaction may be applied to aliphatic esters with equal success, but in this case, with thorium oxide, a certain amount of aldehyde-ammonia is produced, and with aluminium oxide some amide corresponding with the nitrile. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]　　W. G.

New Method of Formation of Nitriles by Catalysis. ALPH. MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 215—217. Compare preceding abstract).—When the mixed vapours of an aldehyde and ammonia are passed over thorium oxide at 420—440°, the products are the corresponding nitrile, water, and some products of condensation of the aldehyde and ammonia. The method has been applied with success both to aliphatic and aromatic nitriles. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]　　W. G.

A New Method of Dehydration of Oximes by Catalysis. ALPH. MAILHE and F. DE GODON (*Bull. Soc. chim.*, 1918, [iv], **23**, 18—20).—Aldoximes were dehydrated by passing their vapour over aluminium oxide or thorium oxide heated at 340—360°, the corresponding nitrile being obtained. Dehydration also occurred under similar conditions with two ketoximes, *iso*butyronoxime and *iso*valeronoxime, the products in these cases being nitriles less rich in carbon.　　W. G.

The Action of Trioxymethylene on the Various Hydrocarbons in the Presence of Aluminium Chloride. G. B. FRANKFORTER (*J. Amer. Chem. Soc.*, 1918, **40**, 329).—A question of priority between Nastjukov and the author. [See A., 1915, i, 227, 953.]　　L. A. C

Extraction of Pure Dimethylnaphthalenes from Coal Tar Oils. GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P., 301079, 1916; from *Chem. Zentr.*, 1917, ii, 713—714).—The neutral purified fraction of the oil, b. p. 260—265°, or the solid hydrocarbon mixture obtainable from this is sulphonated by sulphuric acid, and the resulting sulphonic acids are reconverted into the corresponding parent hydrocarbons.

1:6-Dimethylnaphthalene obtained in this way is a colourless oil of faint characteristic odour, b. p. 265° (*picrate*, needles, m. p. 114°); the sulphonic acid forms a *sulphonamide*, needles, m. p. 185°, on fusion with potassium hydroxide yields a dimethyl-

*g**

naphthol, m. p. 82°, and on reduction with sodium amalgam undergoes scission of the sulphonyl group. Oxidation with dilute nitric acid converts the hydrocarbon into a carboxylic and a dicarboxylic acid, the latter being identical with 1 : 6-naphthalenedicarboxylic acid prepared from 1 : 6-naphthylaminesulphonic acid, whilst the former when heated with hydrochloric acid loses carbon dioxide with formation of 2-methylnaphthalene. Chromic acid oxidises the dimethylnaphthalene to dimethyl-α-naphthaquinone, m. p. 95°, which is further oxidisable by potassium permanganate to o-methylphthalic acid.

2 : 6-Dimethylnaphthalene, leaflets, m. p. 109—110°, b. p. 260—261°, is oxidised by chromic acid to 2 : 6-*dimethyl-α-naphthaquinone*, m. p. 136—137°, and is convertible through the sulphonic acid into a dimethyl-β-naphthol, m. p. 172°.

2 : 7-Dimethylnaphthalene, leaflets, m. p. 96—97°, b. p. 262°, forms a solid sulphonic acid (*sodium* salt, needles), and on oxidation with chromic acid yields a *dimethyl-α-naphthaquinone*, m. p. 114—115°, which is further oxidisable by permanganate to trimellitic acid.   D. F. T.

Separation of Secondary Amines produced in the Catalytic Hydrogenation of Aniline. G. Fouque (*Compt. rend.*, 1917, 165, 1062—1065).

—Catalytic hydrogenation of aniline yields *cyclo*hexylamine, di*cyclo*hexylamine, *cyclo*hexylaniline, and diphenylamine, together with smaller quantities of benzene, *cyclo*hexane, and tar. For the separation of the secondary amines, a method has been based on the following facts. (*a*) Di*cyclo*hexylamine hydrate forms a solid carbonate and three non-hydrolysable sulphates; (*b*) *cyclo*hexylaniline does not form a carbonate, but yields a normal sulphate, a sesquisulphate, and a hydrogen sulphate, which are hydrolysable, but dissolve in water acidified with sulphuric acid; (*c*) aniline does not form a carbonate; (*d*) diphenylamine sulphate has not been isolated. By repeated fractional distillation under ordinary and reduced pressure, the products are separated into fractions, one of which contains only aniline and di*cyclo*hexylamine, and another consists of a mixture of di*cyclo*hexylamine, *cyclo*hexylaniline, and diphenylamine. Each fraction, after the addition of water and ether, is saturated for several hours with carbon dioxide, and the aqueous solution of di*cyclo*hexylamine carbonate is separated, filtered, and neutralised with sulphuric acid. On evaporating the liquid, octahedral crystals of the normal *sulphate* of di*cyclo*hexylamine separate, whilst the *hydrogen sulphate* separates on treating the mother liquors with excess of sulphuric acid. The amine is obtained by dissolving the successive deposits of crystals in water and distilling the solution with sodium hydroxide under reduced pressure. It is a colourless, oily liquid boiling at 135° (under pressure of 20 mm.). The residue from which the di*cyclo*hexylamine carbonate was separated may consist of an ethereal solution of aniline or of a mixture of *cyclo*hexylaniline and diphenylamine with ether. After evaporation of the ether, it is heated with dilute sulphuric

acid, cooled, and filtered, the process being continued so long as the filtrate gives an orange coloration with a mixture of dilute sulphuric and nitric acids. Evaporation of the united filtrates yields deposits of crystals of *cyclo*hexylaniline sesquisulphate, whilst a little di*cyclo*hexylamine hydrogen sulphate may be obtained from the mother liquor. *cyclo*Hexylaniline may be separated from its sesquisulphate by means of warm dilute ammonia solution, and decanting and distilling the oily layer under reduced pressure. It is a strongly refractive liquid, boiling at 157°/20 mm. The solid residue of impure diphenylamine is purified by distillation and crystallisation from ether. C. A. M.

Intermediate Products (Formomethylanilide Derivatives) suitable for the Manufacture of Colouring Matters. H. LEVINSTEIN and G. T. MORGAN (Eng. Pat., 111321, 1916; from *J. Soc. Chem. Ind.*, 1918, 5A).—Formomethylanilide, also its halogen or alkyloxy-derivatives and homologues with a free para-position to the amino-group, may be nitrated at −5° to +20° with formation of the corresponding *p*-nitroformomethylanilide compounds; p-*nitroformomethylanilide* forms pale yellow prisms or needles, m. p. 119—120°. These products on reduction with iron borings and dilute formic or acetic acid at 85—100° are converted into the corresponding *p*-amino-compounds; the unsubstituted p-*aminoformomethylanilide*, $HCO \cdot NMe \cdot C_6H_4 \cdot NH_2$, forms almost colourless needles, m. p. 115—116°. D. F. T.

Reduction of Phenylethylamine. ALBERT WEINHAGEN (*Biochem. J.*, 1917, 11, 272—276).—Phenylethylamine prepared from phenylalanine differs from the synthetic product in that the latter resists reduction by the method of Willstätter and Hatt (A., 1912, i, 545), whilst the former is completely reduced to the hexahydro-compound (*cyclo*hexylethylamine). The synthetic product decolorises permanganate solution very slowly, whilst the other acts almost instantaneously. It is pointed out that Bernthsen remarked certain minor differences between synthetic phenylethylamine and that produced from phenylalanine. [See also *J. Soc. Chem. Ind.*, 1918, March.] J. H. L.

Bromo-alkylated Aromatic Amines. I. J. VON BRAUN, K. HEIDER, and E. MÜLLER (*Ber.*, 1917, 50, 1637—1651).—When methylaniline is heated with ethylene dibromide at 100°, diphenyldiethylethylenediamine is not the only product. The first runnings of the basic distillate contain methyl-β-bromoethylaniline,
$$NMePh \cdot CH_2 \cdot CH_2Br,$$
and the yield of this may be increased to 35% of the methylaniline employed if the proportion of bromide to base is 3 mols. to 2 mols. The new bromo-alkylated base is most remarkably reactive; it can be brominated, nitrated, etc., in the ring like any other tertiary aromatic amine; it has the reactions of tertiary amines in general. but, most important of all, it is capable of all the reactions of ethyl bromide.
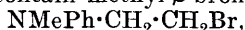
*g** 2

Full details of the economical production of the base are given, together with notes on the recovery of the unchanged ethylene dibromide and methylaniline, and the *tert.*-ethylenediamine. *Methyl-β-bromoethylaniline* is a very pale yellow, somewhat heavy oil, b. p. 140—144°/13 mm., which becomes dark in the air without really suffering much change. The *picrate* has m. p. 125°, and the *methiodide*, m. p. 122°. It reacts with bases as follows: methylaniline gives diphenyldimethylethylenediamine,

$$C_2H_4(NMePh)_2,$$

m. p. 51°; dimethylamine gives *phenyltrimethylethylenediamine*, b. p. 144—146°/23 mm., which forms a *dipicrate*, yellow leaflets, m. p. 171°; trimethylamine yields *β-phenylmethylaminoethyltrimethylammonium bromide*, $NMePh\cdot CH_2\cdot CH_2\cdot NMe_3Br$, as a very hygroscopic, white mass, m. p. 165°. The base may also be brominated or nitrated, giving oily products, but p-*nitrosomethyl-β-bromoethylaniline*, which is prepared exactly like p-nitrosodimethylaniline, is a stable, green mass, m. p. 70°. This reacts with trimethylamine to form a p-nitrosodialkylaniline derivative, $NO\cdot C_6H_4\cdot NMe\cdot C_2H_4\cdot NMe_3Br$, which is soluble in water, the solution having the same green colour as the ethereal solution of p-nitrosodimethylaniline.

Under the influence of aluminium chloride, the base suffers condensation to 1-methyl-2:3-dihydroindole, the yield being about 35%. This is the first instance of the production of a dihydroindole by ring formation, and the method may prove to be of great service in the case of substituted dihydroindoles. By Fittig's method, the base may be converted into *diphenyldimethyltetramethylenediamine*, $C_4H_8(NMePh)_2$, m. p. 81°, b. p. 186—190°/5 mm. (*picrate*, m. p. 173°; *dimethiodide*, m. p. 180°), which gives a brilliant greenish-blue coloration with oxidising agents (compare A., 1917, i, 175).

The base condenses with p-acetylaminophenol under the influence of sodium ethoxide to form ω-*phenylmethylaminophenacetin*, $NHAc\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot NMePh$, in glistening leaflets, m. p. 102°, and with morphine to give ω-*phenylmethylaminodionine*,

$$NMe\dot{:}C_{16}H_{14}O(OH)\cdot O\cdot C_2H_4\cdot NMePh,$$
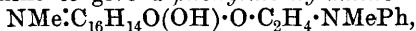
as a yellow oil, which yields a *hydrochloride*, m. p. 110°. These are practically without the physiological action of unsubstituted phenacetin or dionine.

On boiling with aqueous-alcoholic potassium cyanide, the base yields *β-phenylmethylaminopropionitrile*, $NMePh\cdot CH_2\cdot CH_2\cdot CN$, a pleasant-smelling oil, b. p. 186°/23 mm., together with a small quantity of the corresponding *amide*, m. p. 85°. This nitrile is interesting, compared with phenylmethylaminoacetonitrile and other derivatives of aromatic amines containing the grouping $\boldsymbol{:}N\cdot CH_2\cdot CN$, for the basic properties are not masked by the cyano-group, and the *methiodide*, m. p. 132° (decomp.), is stable.

The base reacts with magnesium quite as readily as bromobenzene. When the magnesium compound is decomposed with ammonia and ammonium chloride, it yields methylethylaniline (65%) and diphenyldimethyltetramethylenediamine (35%), and,

strange to say, these are the only products which can be obtained after treating the Grignard compound with ketones, although a vigorous reaction is observed to take place. Aldehydes react in a more normal manner, however, giving bases of the formula

$$NMePh \cdot CH_2 \cdot CH_2 \cdot CHR \cdot OH.$$
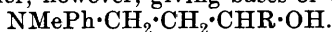
The separation of these from the mixture of products is a matter of considerable difficulty, requiring special methods from case to case. An account is given of the production of the compound $NMePh \cdot C_2H_4 \cdot CHPr^a \cdot OH$ from n-butaldehyde, and its isolation in the form of a *picrate*, long, red needles, m. p. 120°, and *platinichloride*, m. p. 214° (decomp.). The failure of the reaction with ketones recalls the fact that disubstituted amides, $R \cdot CO \cdot NR_2$, react vigorously with organomagnesium compounds, but are regenerated if the products are treated with dilute acids, whilst formamides, $H \cdot CO \cdot NR_2$, give aldehydes. It is suggested that the primary products are additive compounds with quadrivalent oxygen, thus, $R_2 \colon C \colon O <^{MgX}_{R}$, and that in the case of the above base there are steric hindrances against rearrangement into compounds, $R_3C \cdot MgX$.

<div align="right">J. C. W.</div>

Di-n-butylaniline. JOSEPH REILLY and WILFRED JOHN HICKINBOTTOM (T., 1918, **113**, 99—111. Compare this vol., i, 10).—If n-butyl chloride is heated with aniline in an autoclave at 130—140°, a very high yield of mono-n-butylaniline is soon obtained, and if this is heated with more n-butyl chloride at 180° under pressure, a good yield of di-n-butylaniline is produced. This has been converted by normal methods into the following series of compounds: A, p-nitrosodi-n-butylaniline and p-phenylenedi-n-butyldiamine, $C_6H_5 \cdot N(C_4H_9)_2 \longrightarrow NO \cdot C_6H_4 \cdot N(C_4H_9)_2 \longrightarrow NH_2 \cdot C_6H_4 \cdot N(C_4H_9)_2$; B, 4-di-n-butylaminoazobenzene-4′-sulphonate, by means of diazotised sulphanilic acid, and this, by reduction, into the above diamine. Similarly, mono-n-butylaniline has been coupled with diazotised sulphanilic acid and the azo-compound reduced to p-phenylene-n-butyldiamine.

For some unaccountable reason, Karrer was unable to obtain the p-nitroso-compound or to couple the tertiary base with diazotised sulphanilic acid (A., 1915, i, 1073).

Typical salts and other derivatives of these compounds are also described, but the original should be consulted for the details.

<div align="right">J. C. W.</div>

Phototropy and Thermotropy. VIII. Cinnamylideneamines. 2 : 4-Dihydroxybenzylideneamines. ALFRED SENIER and PATRICK HUGH GALLAGHER (T., 1918, **113**, 28—35. Compare A., 1915, i, 397, 877, and earlier).—Various amines have been condensed with cinnamaldehyde and 2 : 4-dihydroxybenzaldehyde in order to gather, if possible, new material for studies on phototropy and thermotropy. Of the many new Schiff's bases thus obtained, nearly all are found to exhibit thermotropic changes, but none are phototropic. Many of them, however,

change permanently into polymorphic forms on exposure to actinic light. Solutions in acetic acid or chloroform are usually deeper in colour than those in light petroleum, benzene, or acetone, and the 2 : 4-dihydroxybenzylidene compounds are green in dilute solutions and yellow in concentrated solutions.

For experimental details, see the original.   J. C. W.

The Sulphonation of β-Naphthylamine. ARTHUR GEORGE GREEN and KAPILRAM H. VAKIL (T., 1918, **113**, 35—44).—It is well known that the 5-, 6-, 7-, and 8-sulphonic acids can be obtained by the direct sulphonation of β-naphthylamine, but it appeared to be of importance in the dye industry to learn something of the mechanism of the reactions, the circumstances favouring the production of the individual isomerides, and the conditions under which one may be converted into another. The present work, therefore, is a detailed study with those aims.

Within temperatures from 20° to 80°, the product contains 97—99·5% of the 5- and 8-acids. The ratio between these does not vary very much from about two parts of the 8-isomeride to three of the 5-acid, neither has time (one to ten hours) nor concentration of the acid (92% H_2SO_4 to an acid with 20% SO_3) much influence on this ratio, except that the lowest temperatures and shortest time are favourable to the production of the 5-acid. At temperatures below 80°, it follows that the sulphonation takes place simultaneously at positions 5 and 8. At higher temperatures and with longer periods of heating there is a falling off in the proportion of the 8-acid and an increased production of the 5-isomeride. This is explained by assuming that the 8-acid suffers hydrolysis to the free β-naphthylamine, which is then resulphonated, mainly to the 5-compound, as above. Simultaneously, the yield of the 6- and 7-isomerides increases also, reaching 7·5% with 96% sulphuric acid at 120° in five hours. It appears probable that disulphonic acids are produced, and that these suffer hydrolysis to monosulphonic acids, the 5-acid giving the 5 : 7- and then the 7-acid, and the 8-isomeride producing the 6 : 8- and then the 6-acid.

For details of the methods of separation and analysis, the original should be consulted.   J. C. W.

Aspirin. V. Action of Salicylsalicylic Acid on the Solidification of Aspirin in Concentric Rings. D. E. TSAKALOTOS and S. HORSCH (*Bull. Soc. chim.*, 1918, [iv], **23**, 16—18).—Salicylsalicylic acid facilitates, but is not essential for, the formation of concentric rings during the crystallisation of aspirin from alcohol.   W. G.

The Indene Series. V. J. VON BRAUN (*Ber.*, 1917, **50**, 1659—1661).—Hydrindone reacts with magnesium methyl iodide to form 1-hydroxy-1-methylhydrindene (A., 1913, i, 1364). This is reconverted into the original ketone by the action of alkalis, which is best demonstrated by leaving methyl-alcoholic solutions of the carbinol with anisaldehyde or *p*-dimethylamino-

benzaldehyde in contact with a few drops of sodium hydroxide, when the known condensation products of hydrindone and the aldehydes soon crystallise out.

1-*Hydroxy*-1-*ethylhydrindene*, $C_6H_4\underset{CEt(OH)}{\overset{CH_2\overline{}}{<}}>CH_2$, a pleasant-smelling syrup, b. p. 123—125°/9 mm., D_4^{20} 1·063, behaves similarly. The tendency to part with the elements of water increases with increasing magnitude of the 1-alkyl group. The methyl compound may be distilled under atmospheric pressure, but the ethyl homologue changes thereby into 1-*ethylindene*, a mobile liquid, b. p. 226°, D_4^{22} 0·9732. With larger radicles, the indenes are already produced during the Grignard reaction, and may be purified by distillation under ordinary pressures. 1-n-*Butylindene*, a very pleasant-smelling liquid, b. p. 252—255°, 120°/10 mm., D_4^{23} 0·9552, and 1-*phenylindene*, $C_6H_4\underset{CPh}{\overset{CH_2}{<}}>CH$, a pale yellow syrup, b. p. 200—201°/29 mm., D_4^{27} 1·0829, may be obtained directly from hydrindone in this way.   J. C. W.

Preparation of 1-Hydroxyanthranol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 301452, 1916; from *Chem. Zentr.*, 1917, ii, 715).—By reducing 1-hydroxyanthraquinone with zinc in acid solution, it is possible to obtain 1-hydroxyanthranol, which is of value as a remedy for psoriasis.   D. F. T.

Triphenylmethyl. XXVIII. Tautomerism of Triarylcarbinols. M. GOMBERG and L. C. JOHNSON (*J. Amer. Chem. Soc.*, 1917, **39**, 1674—1688. Compare A., 1916, i, 639).—The condensation of diphenylmethylene dichloride with phenols is a convenient method for the preparation of *p*-hydroxytriarylcarbinols. It has already been shown that compounds of this class, even if they contain certain substituents in the ortho-position with respect to the phenolic group, exist in two desmotropic forms, benzenoid and quinonoid. From a preliminary survey, however, it appears that substituents in the meta-position in these carbinols (ortho to the central carbon atom) often hinder tautomerism to quinonoid forms.

Thus diphenylmethylene dichloride combines with *m*-cresol to form *diphenyl-5-hydroxy-o-tolylcarbinol*, $OH\cdot CPh_2\cdot C_6H_3Me\cdot OH$, which can only be obtained in the colourless, benzenoid form, m. p. 114°. This has also been synthesised as follows: *m*-cresol and carbon tetrachloride are converted by the Tiemann and Reimer method into 5-hydroxy-*o*-toluic acid, and the ethyl ester of this is treated with magnesium phenyl bromide. The carbinol combines with many solvents, in molecular proportions; *compounds* with acetic acid, alcohol, benzene, chloroform, and carbon tetrachloride are described. The 5-*methylcarbonato*-derivative
$$OH\cdot CPh_2\cdot C_6H_3Me\cdot O\cdot CO_2Me,$$
from methyl chloroformate, has m. p. 118; the 5-*ethylcarbonato*-derivative has m. p. 128°; the 5-*benzoyloxy*-derivative has m. p. 103°; and the 5-*acetoxy*-compound has m. p. 136°. The carbinol loses water at about its m. p., forming *diphenyl-3-methylquino-*
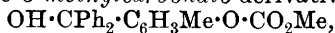
methane, $CPh_2:C_6H_3Me:O$, in red needles, m. p. 183°. This fuchsone absorbs two molecular proportions of hydrogen chloride, one of which is removed by evacuation.

The carbinol is also transformed into the fuchsone hydrochloride when treated with hydrogen chloride, so the triarylmethyl chloride required for the preparation of the free radicle cannot be obtained. The above ethylcarbonato-derivative, however, can be converted into *diphenyl-5-ethylcarbonato-o-tolylcarbinyl chloride*,

$$CO_2Et \cdot O \cdot C_6H_3Me \cdot CPh_2Cl,$$
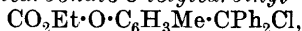
m. p. 96—97°, from which the chlorine can be removed by means of finely divided silver, as usual. The authors have not been able to isolate the free radicle as a solid, but have obtained its *peroxide*, R_2O_2, m. p. 141—142°, by exposing the deep cherry-red, benzene solution to the air until almost bleached and then evaporating.

If the original carbinol is brominated in acetic acid solution, it yields *diphenyl-4 : 6-dibromo-5-hydroxy-o-tolylcarbinol*; this exists as an almost colourless benzenoid modification, m. p. 146·5—147·5°, and in the yellowish-red, quinonoid form, m. p. 147—148°. The latter loses water more rapidly than the former on heating, but both ultimately change at 150° into the dark red *diphenyl-2 : 6-dibromo-3-methylquinomethane*, $CPh_2:C_6HMeBr_2:O$. The corresponding colourless and yellow *diphenyl-4 : 6-dichloro-5-hydroxy-o-tolylcarbinols* have m. p. 135—137°.

m-*Methoxyphenol* also reacts with diphenylmethylene dichloride, giving *4-hydroxy-2-methoxytriphenylcarbinol*, of which only a colourless form, m. p. 132° (decomp.) has been obtained. This crystallises with demi-molecular proportions of benzene and carbon tetrachloride. Its constitution is established by proving that it is not the other possible product, namely, *2-hydroxy-4-methoxytriphenylcarbinol*, which has m. p. 154°, decomp. 158°. This has been synthesised as follows: resorcylic acid is converted by methylation into 2-hydroxy-4-methoxybenzoic acid, and the ethyl ester of this is treated with magnesium phenyl bromide.   J. C. W.

The State of Saturation of Chromophores. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1623—1625. Compare A., 1917, i, 391).—A reply to Lifschitz (A., 1917, i, 558).   J. C. W.

Production of Aminoalkyl Esters and Alkylaminoalkyl Esters of *p*-Aminobenzoic Acid. W. BADER and LEVINSTEIN, LTD. (Eng. Pat., 111328, 1916; from *J. Soc. Chem. Ind.*, 1918, 4—5A).— Alkyl esters of *p*-aminobenzoic acid are heated at 150—180° with an amino- or alkylamino-alcohol in the presence of the aluminium compound of the amino-alcohol, when the simple alcohol is displaced from the ester and distils off; the excess of amino-alcohol may then be removed by distillation in a vacuum. Instead of adding the aluminium derivative of the amino-alcohol as such, it can be formed in the mixture by the addition of aluminium amalgam. *Diethylaminoethyl* p-*aminobenzoate* prepared in this way forms a colourless *hydrochloride*.   D. F. T.

Process for Producing Carbamides and Thiocarbamides of the Aromatic (Benzene or Carbazole) Series. FARBEN-FABRIKEN VORM. F. BAYER & Co. (Eng. Pat., 8591, 1916; from *J. Soc. Chem. Ind.*, 1918, 20A). Carbamide or thiocarbamide compounds can be obtained by the action of carbonyl chloride or thiocarbonyl chloride on aminoacylaminosulphonic acids of the benzene or carbazole series. m-*Nitrobenzoyl*-m-*aminobenzoylaminosulphosalicylic acid*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_2(OH)(SO_3H) \cdot CO_2H,$$

obtained by the action of *m*-nitrobenzoyl chloride on *m*-aminobenzoylaminosulphosalicylic acid, on reduction yields m-*aminobenzoyl*-m-*aminobenzoylaminosulphosalicylic acid*,

$$NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot CO \cdot NH \cdot C_6H_2(OH)(SO_3H) \cdot CO_2H,$$

and this, like bis[*m*-aminobenzoyl]-aminocarbazoledisulphonic acid, can by means of the named reagents be converted into carbamide derivatives possessing valuable therapeutic properties. D. F. T.

The Fluorescence of Cyano-compounds. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1614—1623).—The remarkable fluorescence exhibited by the platinocyanides would lead to the supposition that the cyanogen radicle has a favourable influence on this phenomenon, and makes a study of organic cyanogen compounds particularly interesting. Quite simple nitriles are found to be fluorescent; benzonitrile, for example, is strongly reactive in the ultra-violet. 2 : 5-Dimethoxybenzonitrile might therefore be expected to be very fluorescent, as it combines the properties of very fluorescent *p*-dimethoxybenzene with those of the cyano-group. As a matter of fact, the eye can scarcely detect any fluorescence (compare Grignard, Bellet, and Courtot, A., 1916, i, 487), but in the ultra-violet $N/1000$-alcoholic solutions are most strongly fluorescent. *o*-Aminobenzonitrile should also be very active, but no mention of the property has been made in the literature. Alcoholic solutions exhibit a powerful violet fluorescence, which is displaced towards the ultra-violet in indifferent solvents. Among more complicated nitriles, a number of striking examples have recently been described (A., 1917, i, 394).

It is remarkable that many organic cyanogen compounds are only fluorescent in the solid state, like barium platinocyanide. The compound $NMe_2 \cdot C_6H_4 \cdot CH \vdots CPh \cdot CN$ (*ibid.*) is an example of this. The corresponding free amino-compound, $NH_2 \cdot C_6H_4 \cdot CH \vdots CPh \cdot CN$, is also only fluorescent in the solid state, but the isomeride,

$$NH_2 \cdot C_6H_4 \cdot C(CN) \vdots CHPh,$$
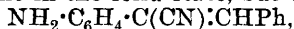
is strongly active both in the solid form and in solution. The intimate connexion between fluorescence and constitution is here exemplified in a new way.

The last-named compound is a representative of a new class of substances which are strongly fluorescent in solution, namely, compounds containing the group $-CH \vdots C(CN) \cdot C_6H_4 \cdot NH_2$, of which examples are now given.

Nitro-groups are generally a hindrance to fluorescence, but the

cyano-group can often overcome this influence. Thus, the compounds $OMe \cdot C_6H_4 \cdot CH:C(CN) \cdot C_6H_4 \cdot NO_2$ and

$$C_6H_4[CH:C(CN) \cdot C_6H_4 \cdot NO_2]_2$$

are fluorescent, at any rate in the solid state, whilst the analogous substances free from the cyano-group are very feebly active.

Red compounds, as a rule, are likewise seldom fluorescent, but even red nitriles are known which are brilliantly fluorescent. When viewed in the light of a mercury lamp behind a blue screen so arranged that substances like lead chromate or cinnabar appear to be black, the red compound, $NMe_2 \cdot C_6H_4 \cdot CH:C(CN) \cdot SO_2Ph$ (Tröger and Bremer, A., 1910, i, 113), shines with a vermillion light; the red nitrile, $NMe_2 \cdot C_6H_4 \cdot CH:CBz \cdot CN$ (*loc. cit.*), appears to be brick-red; *p*-dimethylaminobenzylidenemalonitrile is orange-red, and the compound, $NMe_2 \cdot C_6H_4 \cdot N:CPh \cdot CN$ (Ehrlich and Sachs, A., 1899, i, 883), appears to be bright brick-red.

[With AD. JEUTTER.]—*α*-p-*Aminophenylcinnamonitrile* (p-*amino-α-cyanostilbene*), yellow crystals, m. p. 122°, blue fluorescence in benzene, ether, or chloroform, green in alcohol, bluish-violet in carbon tetrachloride or light petroleum, is obtained by reduction of the nitro-compound, which is prepared by the condensation of *p*-nitrobenzyl cyanide with benzaldehyde.

α-p-*Aminophenyl-γ-benzylideneacrylonitrile* (*α*-cyano-*α*-amino-phenyl-δ-phenylbutadiene), which forms pale brown crystals, m. p. 153°, is obtained by reduction of the product of the condensation of cinnamaldehyde with *p*-nitrobenzyl cyanide. The fluorescence exhibited is as follows: solid, feebly red behind the blue screen; solution in pyridine or acetone, bright green; in glacial acetic acid, ether, or chloroform, greenish-blue; in alcohol, yellowish-green; in light petroleum, violet-blue; even in such an unfavourable solvent as carbon disulphide, a blue fluorescence is still manifest.

Dinitro-α : α'-dicyanodistyryl-4 : 4'-benzene,

$$C_6H_4[CH:C(CN) \cdot C_6H_4 \cdot NO_2]_2,$$
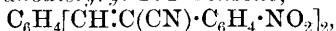
yellow crystals, m. p. above 300°, is formed by condensing *p*-nitrobenzyl cyanide with terephthalaldehyde.

[With (FRL.) LILLY LUTZ.]—p-*Amino-α-phenylcinnamonitrile* (p-*amino-ω-cyanostilbene*), from the nitro-compound, forms yellow crystals, m. p. 143°. *α*-p-*Aminophenyl-2-methoxycinnamonitrile*, stout, yellow needles, m. p. 105°, is obtained from the *nitro*-compound, $OMe \cdot C_6H_4 \cdot CH:C(CN) \cdot C_6H_4 \cdot NO_2$ (lemon-yellow needles, m. p. 190°, brilliant lemon-yellow fluorescence behind the blue screen), which is prepared by the action of *p*-nitrobenzyl cyanide on *o*-methoxybenzaldehyde. *α*-p-*Aminophenyl-4-methoxycinnamonitrile* forms yellow needles, m. p. 151°, and its fluorescence is as follows: solid, moderate greenish-yellow; solutions in pyridine and alcohol, green, in acetone, blue, and in ether, violet-blue. *α*-p-*Aminophenyl-3 : 4-methylenedioxycinnamonitrile*,

$$CH_2:O_2:C_6H_3 \cdot CH:C(CN) \cdot C_6H_4 \cdot NH_2,$$
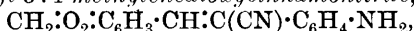
yellow needles, m. p. 174° (intense bluish-green fluorescence in pyridine), is obtained from the corresponding *nitro*-compound, yellow needles, m. p. 188° (strong orange-yellow fluorescence),

which is prepared by the condensation of p-nitrobenzyl cyanide and piperonaldehyde. 　　　　　　　　　　　　　　　　　　J. C. W.

Mandeliminohydrin. JOHN EDWIN MACKENZIE (T., 1918, **113**, 1—3).—Following Eschweiler's method for the preparation of "iminohydrins" of α-hydroxy-acids (A., 1897, i, 399), the author has converted benzaldehydecyanohydrin into the iminoalkyl ether hydrochloride, $OH \cdot CHPh \cdot C(OEt) \colon NH, HCl$, and this by means of silver hydroxide into "*mandeliminohydrin*," m. p. 173—179° (decomp.) (see following abstract). 　　　　　　　　　　J. C. W.

Amidine Salts, and the Constitution of the so-called Iminohydrins. HAROLD GORDON RULE (T., 1918, **113**, 3—20).— The iminohydrins or *iso*amides, which are usually prepared by the action of moist silver oxide on imino-ether hydrochlorides, or water on the free imino-ethers, were formulated by Eschweiler as $OH \cdot CR \colon NH$ (A., 1897, i, 399) and by Hantzsch as

$$NH \colon CR \cdot O \cdot NH_2 \colon CR \cdot OH$$
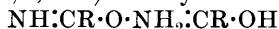
(A., 1901, i, 676). Hantzsch showed that the compounds are comparatively strong electrolytes, with molecular weights twice as great as Eschweiler supposed. "Glycolliminohydrin" hydrochloride and the sodium salt of "glycolliminohydrin" are, moreover, known to be considerably hydrolysed in aqueous solutions, and Walker, under whose inspiration the present paper and Mackenzie's note (preceding abstract) have been presented, finds that the degree of hydrolysis for $N/8$-solutions is about 50%. On the theory of amphoteric electrolytes, therefore, free "iminohydrins" should be very feeble conductors, but their conductivities are really as high as that of a salt, which is in conflict with Hantzsch's formula.

Hantzsch and Walker were both impressed with the fact that all "iminohydrins" described so far have been those of α-hydroxy-acids. The hydroxyl group is not a critical part of the molecule, however, for the methoxyacetic and phenylacetic derivatives have now been obtained, and the discovery has been made that the compounds are really amidine salts of the formula

$$NH_2 \cdot CR \colon NH, R \cdot CO_2H.$$

Thus, "glycolliminohydrin" is glycollamidine glycollate, and "mandeliminohydrin" is mandelamidine mandelate,

$$OH \cdot CHPh \cdot C(NH_2) \colon NH, CO_2H \cdot CHPh \cdot OH.$$

These two salts have been synthesised by the interaction of the amidine hydrochlorides and sodium glycollate or mandelate, as the case may be.

The hydrolysis of the imino-ethers by water is formulated thus: (1) $OEt \cdot CR \colon NH + 2H_2O = R \cdot CO_2NH_4 + EtOH$; (2) $R \cdot CO_2NH_4 + OEt \cdot CR \colon NH = NH_2 \cdot CR \colon NH, R \cdot CO_2H + EtOH$. In this connexion, it is interesting to note that imino-ethers react with ammonium chloride, but not ammonia, to form amidine hydrochlorides (Knorr, A., 1917, i, 255).

In examining amidine salts of the hydroxy-acids, a number of Eschweiler's statements have been revised.

For experimental details, see the original.   J. C. W.

Influence of the Replacement of a β-Hydrogen Atom by a Phenyl Group in α-Hydroxy-γ-phenylcrotonic and γ-Hydroxy-γ-phenylcrotonic Acids. J. BOUGAULT (*Bull. Soc. chim.*, 1918, [iv], **23**, 20—24).—The introduction of a β-phenyl-group into these acids considerably modifies the molecule, in that it prevents the reactions which are apparently the most character-istic of the groupings ·CH:CH·CH(OH)·CO₂H and ·CH(OH)·CH:CH·CO₂H.

Thus the reactions with alkalis, mineral acids, oxalic acid, iodine in excess, and sodium carbonate are all modified.   W. G.

Nitration of 5- and 6-Acetylamino-3 : 4-dimethoxybenzoic Acids and 4-Acetylaminoveratrole. JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1918, **113**, 22—28).—The authors have recently been associated with Gibson in a study of the nitra-tion of 2-acetylamino-3 : 4-dimethoxybenzoic acid and 3-acetylamino-veratrole (A., 1917, i, 203), and the present work is a natural sequel.

5-Acetylamino-3 : 4-dimethoxybenzoic acid, prepared from 5-nitrovanillin, yields the 6-nitro-compound, which may be con-verted into the known 6-nitroveratric acid, and also some 4 : 5-di-nitro-3-acetylaminoveratrole (*ibid.*). In the case of 6-acetylamino-3 : 4-dimethoxybenzoic acid, the carboxyl group is displaced on nitration, the sole product being 5-nitro-4-acetylaminoveratrole, which may also be prepared by nitrating 4-acetylaminoveratrole, and can be converted into 4-nitroveratrole.

For experimental details, see the original.   J. C. W.

Camphoceanaldehydic Acid (*tert.-sec.*) (**Camphoric Acid Semialdehyde**). **II.** J. BREDT (*J. pr. Chem.*, 1917, [ii], **96**, 65—72. See also A., 1917, i, 560).—Camphoraldehydic acid is unstable both in its active and inactive modifications; not only does it readily undergo atmospheric oxidation, but also, when kept out of contact with air, the crystalline acid gradually becomes liquid, the alteration apparently being one of polymerisation. The aldehydic acid is therefore conveniently kept in the form of its acetyl derivative, viz., acetoxy-β-campholide, from which it is easily reobtained by hydrolysis with aqueous sodium carbonate.

[With L. ACKERMANN and J. DORREN.]—If *d*-camphoraldehydic acid is heated for eight hours at 100° in a sealed tube with acetic anhydride, the normal *l*-acetoxy-β-campholide, m. p. 126—128°, is obtained, together with an *isomeride*, prisms or tablets, m. p. 81—83°, $[α]_D^{28} + 95·77°$ in benzene; both products on hydrolysis with sodium carbonate yield the original aldehydic acid. In a similar manner, *dl*-camphoraldehydic acid on prolonged heating with acetic anhydride gives rise to a mixture of the *dl*-acetoxy-campholide, m. p. 97—98°, already described (*loc. cit.*), together with an *isomeride*, tablets, m. p. 73—74°. The active and inactive compounds already known, together with their isomerides now

described, do not reduce potassium permanganate in neutral aqueous solution, and therefore are all free from the aldehydic group; the isomerism is therefore regarded as similar to that of the *endo-* and *exo-*borneols, and due to the position of the acetoxy-group with respect to the plane of the six-atom ring.

The failure of Rupe and Splittgerber (A., 1907, i, 1016) to obtain β-campholide by the action of nitrous acid on β-aminocampholic acid is ascribed to the conversion of the four-atom ring into a five-atom ring during the reaction, according to which view the liquid product of this reaction is to be regarded as the lactone of hydroxy-trimethyl*cyclo*hexanecarboxylic acid; such enlargements of the four-atom ring have already been observed (Demjanoff and Luschnikoff, A., 1903, i, 403; Errera, A., 1893, i, 108; 1894, i, 202).

In order to avoid the inconveniently high temperature (erroneously quoted as 600° instead of 400° in the earlier paper) necessary for the production of sodamide, a mixture of sodamide and potassamide is prepared by passing ammonia on to a mixture of the metals (2:1 by weight) at 270—280°. D. F. T.

Preparation of α-Naphtholphthalein. EMIL ALPHONSE WERNER (T., 1918, **113**, 20—21).—A mixture of α-naphthol, phthalic anhydride, and a small quantity of sulphuric acid is carefully heated at 60—65°. The yield is about 33% of the weight of α-naphthol, but is seriously diminished if the temperature rises above 65°.

J. C. W.

Production of Anils of Hydroaromatic Ketones. GUSTAV REDDELIEN (D.R.-P., 301121, 1915; from *Chem. Zentr.*, 1917, ii, 714).—Anils are easily obtained by heating the hydroaromatic ketones with amino-compounds at 160—180° in the presence of a small quantity of a strong acid, for example, hydrochloric acid, as catalyst; instead of the acid, the corresponding salt of the amino-compound may be used, or, if the reaction is vigorous, even a metallic salt, for example, the zinc salt of the acid may be applied. Camphor when heated with aniline and aniline hydrochloride yields *camphoranil*, colourless needles, m. p. 13·5°, b. p. 164—165°/ 15 mm.; menthone and aniline react in the presence of the additive compound of zinc chloride and aniline, giving *menthoneanil*, a pale yellow oil, b. p. 162—172°/16 mm., whilst with *p*-anisidine, *menthone-p-anisil*, m. p. 61—62°, is formed; *carvoneanil*, obtained similarly, is a yellow oil, b. p. 179—181°/15 mm., which forms an exceptionally sensitive reagent for nitric acid, giving a deep blue coloration with this substance. D. F. T.

Decomposition of Oximinocamphor when Heated. E. SERNAGIOTTI (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 221—223). —Beckmann and Köster (A., 1893, i, 474) showed that, on fusion, α-benziloxime is converted into benzoic acid and benzonitrile, the hydroxyl of the :C:N·OH group passing to the adjacent carbonyl group. On the other hand, Kötz and Wunstorf (A., 1913, i, 1361) found that at 240° oximinocamphor is decomposed in a different manner, the products formed being dimethylheptenonitrile and

camphoric anhydride, although the grouping undergoing change is the same as in the previous case, namely, $:C\cdot CO\cdot C(:NOH)\cdot C:$. The authors find, however, that at 206—207° oximinocamphor is rapidly decomposed with formation of the α-nitrile of camphoric acid, together with a green oil of ketonic or aldehydic character; the nitrile results from a reaction similar to that occurring with α-benziloxime.   T. H. P.

Constituents of Ethereal Oils. Synthetical Experiments in the Unicyclic Sesquiterpene Series. F. W. SEMMLER, K. G. JONAS, and K. OELSNER (*Ber.*, 1917, **50**, 1838—1842).—The product of the action of magnesium *iso*amyl iodide on carvone contains not only *iso*amyl-α-dehydrophellandrene (following abstract), but small quantities of oxygenated compounds with higher b. p.'s.

CMe:CH₂
|
CH
CH₂ CH₂
CH C<CH₂·CH₂·CHMe₂ / OH
CMe
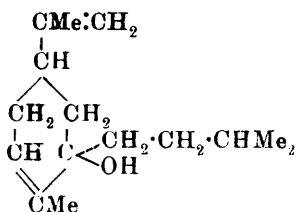
One of these is the normal carbinol, tert-*iso*amylcarveol (annexed formula), which has b. p. 155—170°/12 mm., D^{20} 0·9217, n_D^{20} 1·4917, α_D^{20} $-4°$, and is the first synthetic unicyclic sesquiterpene alcohol. It loses water when treated with potassium hydrogen sulphate, and may be hydrogenated to form tert.-*iso*amyltetrahydrocarveol, b. p. 154—160°/17 mm., D^{20} 0·8908, n_D^{20} 1·4632, α_D^{20} $-1·5°$.

The other compound, which is formed in larger quantity if ether is used instead of benzene as the solvent, is the first synthetic sesquiterpene ketone. The *iso*amyl group is introduced at the double linking in the carvone ring instead of at the carbonyl group.

CMe:CH₂
|
CH
CH₂ CH₂
CO CH·CH₂·CH₂·CHMe₂
CHMe
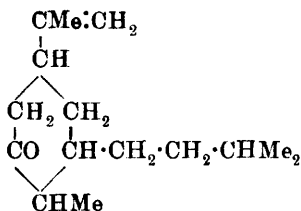
*iso*Amyldihydrocarvone (annexed formula) has b. p. 144—148°/10 mm., D^{20} 0·9022, n_D^{20} 1·47694, α_D^{20} $-8°$, forms an *oxime*, m. p. 135°, and may be reduced by sodium and alcohol to sec-*iso*amyldihydrocarveol. This b. p. 150—155°/10 mm., D^{20} 0·8993, n_D^{20} 1·47449, α_D^{20} $+1°$, forms an *acetate*, b. p. 155—160°/11 mm., D^{20} 0·9227, n_D^{20} 1·46711, α_D^{20} $+5°$, and may be

hydrogenated to sec.-*iso*amyltetrahydrocarveol, b. p. 145—152°/12 mm., D^{20} 0·8906, n_D^{20} 1·46855, α_D^{20} $+1°$. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]   J. C. W.

Constituents of Ethereal Oils. Gum Ammoniac Oil, and Synthetical Experiments on the Nature of its Constituents. F. W. SEMMLER, K. G. JONAS, and PAUL ROENISCH (*Ber.*, 1917, **50**, 1823—1837).—I. *Investigation of Gum Ammoniac Oil.*—The gum-resin, which is obtained in the first instance as a milky juice, from the umbelliferous plant *Dorema ammoniacum* and several *Ferula* species, yields about 0·3% of an oil on distillation. A sample of this, with D^{20} 0·8855, n_D^{20} 1·47233, and α_D^{20} $+1·7°$, has been submitted to a thorough investigation along the usual lines. The first two fractions, b. p. 60—130°/10 mm., 19% of the oil, contain linalyl and citronellyl acetates. The third fraction, b. p. 130—140°/

10 mm., 20% of the oil, consists chiefly of a unicyclic, dihydro-sesquiterpene, $C_{15}H_{26}$, to which the name *ferulene* is given; this has not been obtained pure, as the sample contains about 25% of a bicyclic sesquiterpene, $C_{15}H_{24}$, the constants, b. p. 124—126°/7 mm., D^{20} 0·8698, n_D^{20} 1·48423, $a_D^{20} + 6°$, being in agreement with such a mixture; on reduction it yielded *tetrahydroferulene*, b. p. 118—120°/10 mm., D^{20} 0·8400, n_D^{20} 1·45810, $a_D^{20} + 4·2°$. About 22% of the oil was found to have b. p. 145—155°/12 mm., D^{20} 0·8765, n_D^{20} 1·47160, $a_D^{20} + 3·5°$, and to consist of an ethylenic, sesquiterpene ketone, to which the name *doremone* is assigned. This is the first record of a ketone of this class, either among natural or synthetic compounds. Doremone, $C_{15}H_{26}O$, forms an *oxime*, m. p. 88°, b. p. 160—185°/10 mm., D^{20} 0·8995, n_D^{20} 1·47914, $a_D^{20} + 2°$ (*acetate*, b. p. 180—195°/9 mm., D^{20} 0·9283, n_D^{20} 1·47370, $a_D^{20} + 1°$), and a *semicarbazone*, m. p. 124°. It may be reduced by means of platinum and hydrogen to *tetra-hydrodoremone*, $C_{15}H_{30}O$, b. p. 142—144°/12 mm., D^{20} 0·8434, n_D^{20} 1·44803, $a_D^{20} + 1·4°$, and by means of sodium and alcohol to the ethylenic alcohol, *doremol*, $C_{15}H_{28}O$, b. p. 145—150°/12 mm., D^{20} 0·8702, n_D^{20} 1·47130, $a_D^{20} + 3°$, which may be further reduced by platinum and hydrogen to *tetrahydrodoremol*, $C_{15}H_{32}O$, b. p. 140—145°/12 mm., D^{20} 0·8403, n_D^{20} 1·44818, $a_D^{20} + 2·8°$, a paraffin alcohol with abnormal carbon chain. *Doremyl acetate*, b. p. 155—165°/12 mm., D^{20} 0·8896, n_D^{20} 1·46596, $a_D^{20} + 4·8°$, is also present in the higher fractions. The highest fraction, b. p. above 175°/12 mm., contains cetyl alcohol, which has not hitherto been found in plants.

II. *Experiments on the Synthesis and Characterisation of Uni-cyclic and Olefinic Compounds of the Sesquiterpene Series.*—When carvone is treated with magnesium *iso*amyl iodide in benzene, it yields a unicyclic sesquiterpene, the intermediate carbinol readily losing the elements of water, thus:
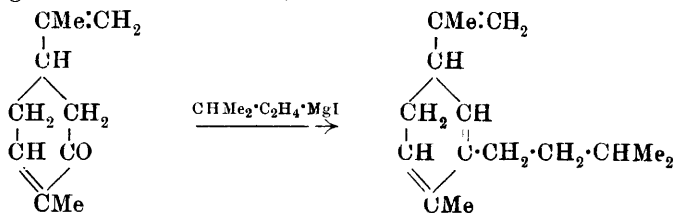
The hydrocarbon, *isoamyl-a-dehydrophellandrene*, has b. p. 130—132°/11 mm., D^{20} 0·8679, n_D^{20} 1·49478, $a_D^{20} + 18·5°$, does not form a solid compound with hydrogen chloride or suffer condensation to a bicyclic compound, which shows the absence of conjugated double linkings in the side chain, but it combines with six atomic proportions of hydrogen to form *isoamylmenthane*, $C_{15}H_{30}$, b. p. 131—133°/14 mm., D^{22} 0·8250, n_D^{22} 1·45562, $a_D^{12} - 1·5°$.

Farnesol may be hydrogenated in the presence of platinum to form inactive *hexahydrofarnesol*, $C_{15}H_{32}O$, b. p. 145—155°/15 mm., D^{22} 0·8387, n_D^{20} 1·44525, with which the above doremol is obviously closely connected. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]

J. C. W.

The Essential Oil of Sea-samphire from different parts of France. MARCEL DELÉPINE and GASTON DE BELSUNCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 24—35. Compare A., 1909, i, 642; 1910, i, 401).—The results of the analyses of oil of samphire (*Crithmum maritimum*) obtained from plants grown in different parts of France show that they all contain the characteristic constituents, namely, 5 : 6-dimethoxy-3 : 4-methylenedioxy-1-allylbenzene, the methyl ether of thymol, and crithmene. In some cases *p*-cymene and *d*-pinene, and a paraffin, m. p. 63°, were also obtained. [See also *J. Soc. Chem. Ind.*, 1918, 137A.]   W. G.

The Colloidal Nature of Colophony. II. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 148—154. Compare this vol., i, 25). —Further observations which are said to be of interest in reference to the colloidal nature of resin. [See, further, *J. Soc. Chem. Ind.*, 1918, 130A.]   H. M. D.

Natural Resins [Überwallungsharze]. IX. MAX BAMBERGER and HERBERT VON KLIMBURG (*Monatsh.*, 1917, **38**, 457. See also Bamberger and Renezeder, A., 1903, i, 643; 1899, i, 929; 1898, i, 88).—The resin obtained from the stone pine (*Pinus cembra*) possesses an odour recalling vanillin, becomes reddened on exposure to light, and has m. p. about 70°, acid number 127, and iodine number 112, but the value for the last is as low as 78·4 if the resin is previously purified by dissolving in alcohol and pouring into water acidified with hydrochloric acid; the methoxyl content is lower than in other natural resins, amounting only to 13 parts per 1000. Boiling water extracts from the resin caffeic acid and also small quantities of ferulic acid and vanillin, whilst the residual molten resin on fusion with potassium hydroxide yields *p*-hydroxybenzoic acid, catechol, protocatechuic acid, acetic acid, and a trace of butyric acid. As with the resins investigated earlier, stone pine resin, after extraction with water, can be separated into an α-resin soluble in ether and a β-resin insoluble in the same solvent, the α-resin, which has a much lower methoxyl content than the β-resin, predominating. Attempts to produce a resinol analogous to pinoresinol or lariciresinol (Bamberger, A., 1894, i, 109) were unsuccessful.

Lariciresinol when heated with zinc dust in a stream of hydrogen yields a distillate containing toluene, xylene, naphthalene, methylnaphthalene, a trace of guaiacol, and probably also cumene. Lariciresinol also gives a resinous ozonide, but the only decomposition product identified after shaking with water was hydrogen peroxide.

Pinoresinol is already known to contain two hydroxyl groups; by heating with alcohol and a little sulphuric acid, it can be converted into an amorphous *anhydro*-compound, $C_{19}H_{18}O_5$, which resists the action of methyl sulphate in alkaline solution, but on treatment with acetyl chloride yield diacetylpinoresinol.

                                        D. F. T.

The Aloins. II. E. LÉGER (*Ann. Chim.*, 1917, [ix], **8**, 265—302. Compare A., 1917, i, 276).—A résumé of work already published

(compare A., 1912, i, 708; 1914, i, 309, 707; 1915, i, 889; 1916, i, 413).   W. G.

Synthesis in the Pyran Series. J. VON BRAUN and Z. KÖHLER (*Ber.*, 1917, **50**, 1657—1658).—$\beta\beta'$-Di-iodoethyl ether has already been used in the synthesis of compounds containing the morpholine ring (I) (compare Clarke, T., 1912, **101**, 1788). It may also be applied to the preparation of pyran derivatives of the type (II).

$$O{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}N\cdot \qquad\qquad O{<}^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}{>}C{<}$$

(I.)   (II.)
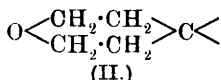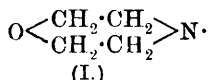
Thus, ethyl disodiomalonate and $\beta\beta'$-di-iodoethyl ether react to form *ethyl tetrahydropyran-4 : 4-dicarboxylate*, b. p. 152—155°/21 mm. The free *acid* crystallises in colourless leaflets, m. p. 172—173°, and yields *tetrahydropyran-4-carboxylic acid*, m. p. 87°, when heated above its m. p.   J. C. W.

Action of Hydrobromic Acid on Cinchonine and its Isomerides : Cinchoniline, Cinchonigine, and *apo*Cinchonine. E. LÉGER (*Compt. rend.*, 1918, **166**, 76—79. Compare Cordier von Löwenhaupt, A., 1899, i, 176).—When cinchonine or its isomerides are heated on a water-bath with hydrobromic acid (D 1·49), there is addition of hydrogen bromide, but at the same time isomerisation occurs. Thus, in the case of cinchonine, the mother liquors, after the separation of hydrobromocinchonine, contain cinchonigine, δ-cinchonine, *apo*cinchonine, cinchoniline in small amount, and an amorphous base, which the author names *cinchoniretine*, which is isomeric with cinchonine. From cinchonigine and *apo*cinchonine no cinchoniline was obtained. Further, although the four isomeric bases give the same hydrobromocinchonine, with cinchonigine and *apo*cinchonine there is a simultaneous formation of *hydrobromo*apo*cinchonine.*   W. G.

Preparation of Derivatives of Alkaloids of the Cocaine Group. CHEMISCHE WERKE GRENZACH (D.R.-P., 301139, 1915 ; from *Chem. Zentr.*, 1917, ii, 714—715).—The compounds derived from alkaloids of the cocaine group by demethylation at the nitrogen atom, for example, anhydronorecgonine (tropene-2-carboxylic acid, annexed formula) and anhydrodihydronorecgonine (tropane-2-carboxylic acid) and their esters, on alkylation at the nitrogen atom by means of halogen-alkyl benzoates, yield compounds of marked pharmacological activity, showing similar properties to cocaine; they possess great local anæsthetic power, and are also sterilisable and less poisonous than cocaine. The ethyl ester of anhydroecgonine on treatment with cyanogen bromide and subsequent hydrolysis is convertible into anhydronorecgonine, of which the *ethyl* ester, b. p. 148—151°/20 mm., reacts with γ-bromopropyl benzoate, with formation of oily *benzoxypropylanhydronorecgonine*
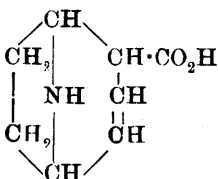
ethyl ester; *hydrochloride*, crystals, m. p. 116—117°. γ-Bromo-propyl *p*-nitrobenzoate, m. p. 42°, b. p. 229—233°/17 mm., reacts with the ethyl ester of anhydronorecgonine, yielding p-*nitrobenz-oxypropylanhydronorecgonine ethyl ester*, $C_{20}H_{24}O_6N_2$; *hydro-chloride*, hygroscopic crystals, m. p. 154°; *picrate* difficulty crystal-lisable. On reduction with tin and hydrochloric acid, the nitro-compound is converted into p-*aminobenzoxypropylanhydro-norecgonine ethyl ester*, $C_{20}H_{26}O_4N_2$; *hydrochloride*, hygroscopic and of no definite m. p.; *platinichloride*, m. p. 297°; *aurichloride*, m. p. 93°. ε-Bromoamyl benzoate and anhydronorecgonine ethyl ester react with formation of *benzoxyamylanhydronorecgonine ethyl ester* (*hydrochloride*, oily). Anhydrodihydronorecgonine ethyl ester, b. p. 135—138°, obtained by the reduction of anhydronor-ecgonine ethyl ester with hydrogen in the presence of a catalyst, reacts with γ-bromopropyl benzoate, giving *benzoxypropylanhydro-dihydronorecgonine ethyl ester*, $C_{20}H_{27}O_4N$; *hydrochloride*, m. p. 142°; *platinichloride*, m. p. 94—95°; *aurichloride*, m. p. 127—128°.

D. F. T.

The Rotatory Power and Molecular Weight of Gitaline (ψ-Digitoxine). JAMES BURMANN (*Bull. Soc. chim.*, 1917, [iv], **21**, 290—293).—The author finds for gitaline carefully prepared and purified the values $[\alpha]_D^{15} - 25.2°$ (in chloroform) and $- 18.8°$ (in alcohol), and for the molecular weight 539, by the ebullioscopic method, chloroform being the solvent. [See also *J. Soc. Chem. Ind.*, 1918, 136A.]

W. G.

Constitution of the Morphine Alkaloids. Synthesis of *iso*Quinoline Derivatives. II. ADOLF KAUFMANN and NICLAUS DÜRST (*Ber.*, 1917, **50**, 1630—1637. Compare A., 1916, i, 502).—According to Knorr's researches on the morphine alkaloids, they are not *iso*quinoline derivatives, but yield such when heated with concentrated hydrochloric acid or zinc chloride solution, that is, by the rupture of the seven-membered nitrogen ring and closure of a new ring. This is illustrated by the change from morphine to *apo*morphine, thus:
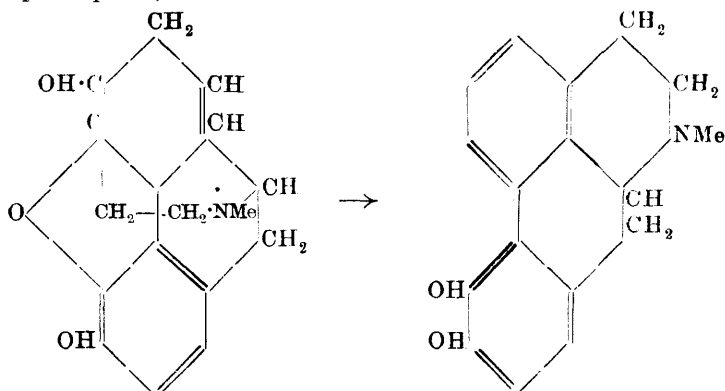
After rupture of the "morphine" ring, and before closure to the *iso*quinoline nucleus, one of the three chains ·NMe·CH₂·CH₂·OH, ·NMe·CH₂·CH₂Cl, or ·NMe·CH:CH₂ might be present. In order to gain some idea as to the possibility of the first of these being formed, the authors have synthesised piperonyl-β-hydroxyethyl-methylamine (I), and attempted to condense it to dihydro-hydrastinine (II). Unlike the tertiary phenylethylamine (III), however, the *tert*.-benzylamine does not yield an *iso*quinoline.

$CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot NMe\cdot CH_2\cdot CH_2\cdot OH \xrightarrow{\ doe\ s_{not}\ }$
(I.)

$. CH_2\!\!<\!^O_O\!\!>$

$CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot CH_2\cdot NMe\cdot CH_2\cdot OH \xrightarrow{\ does\ }$
(II.)

(III.)
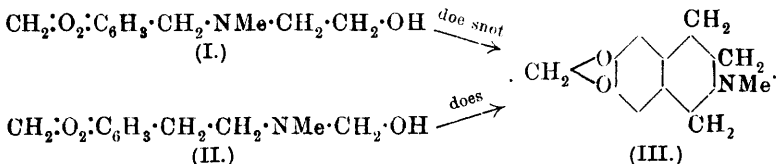
This is probably due to the ease with which *tert*.-benzylamines decompose into benzyl alcohol and *sec*.-amines (Tiffeneau and Fuhrer, A., 1914, i, 517), for the present base is broken down on boiling with acetic anhydride into the compounds
$$CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot OAc$$
and $NMeAc\cdot C_2H_4\cdot OAc$.
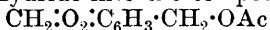
Piperonaldehyde and methylamine are condensed to piperonyl-idenemethylamine, b. p. 128—129°/10·5 mm. (Andree, A., 1902, i, 210); this is reduced to piperonylmethylamine, b. p. 126·5°/10 mm., by means of hydrogen and spongy platinum, and this is condensed with ethylene oxide to 3 : 4-*methylenedioxybenzylmethyl-β-hydroxyethylamine* (I), b. p. 172—173°/10 mm. No agents have been found which can bring about the condensation of this base to dihydrohydrastinine (II). Hydrochloric acid at 100° converts it into the salt, $CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot NMe\cdot CH_2\cdot CH_2Cl,HCl$, and this also yields no dihydrohydrastinine, even when treated with zinc dust or aluminium chloride. On heating at 100°, the free chloro-base changes into *dipiperonylpiperazine dimethochloride*,

$$CH_2\!:\!O_2\!:\!C_6H_3\cdot CH_2\cdot NMe\!\!<\!^{CH_2\cdot CH_2}_{CH_2\cdot CH_2}\!\!>\!NMe\cdot CH_2\cdot C_6H_3\!:\!O_2\!:\!CH_2,$$
$$\overset{\bullet}{Cl}\qquad\qquad\qquad\overset{\bullet}{Cl}$$
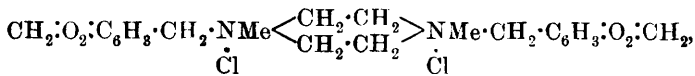
m. p. 221° (decomp.) (*picrate*, m. p. 212°). [See also *J. Soc. Chem. Ind.*, 1918, 136A.] J. C. W.

Reactions of Piperidine with Organic Halogen Compounds in Ethereal Solutions. SARGENT G. POWELL and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1917, **39**, 1717—1723).—When reaction takes place between piperidine and organic haloids in dry ether, the primary products are additive compounds, being, in fact, the halogen hydracid salts of the *N*-derivatives of piperidine. These differ in stability towards water, heat, and bases, and decompose ultimately into the piperidine salt and substituted bases, thus: $C_5H_{10}NH + RX \longrightarrow C_5H_{10}NR,HX \longrightarrow C_5H_{10}NR + HX$; $C_5H_{10}NH + HX \longrightarrow C_5H_{10}NH,HX$. The salts are obviously

obtained as precipitates, which are sometimes nearly pure additive products, sometimes nearly pure piperidine salts, but usually mixtures. The lower alkyl haloids react so quickly and in the dark that they give the purest additive compounds; iodides react more smoothly than bromides, and these more readily than chlorides. From the halogen estimation, the percentage of additive compound (*A.C.*) in the precipitate can be roughly estimated.

Methyl iodide gave pure 1-methylpiperidine hydriodide; *iso*propyl bromide gave piperidine hydrobromide; *iso*butyl iodide gave 1-*isobutylpiperidine hydriodide*, stout, prismatic needles, m. p. 131°; *iso*amyl chloride gave a precipitate containing 84% of *A.C.*; *iso*amyl bromide gave *A.C.* 0·8%; *iso*amyl iodide gave *A.C.* 61·5%; cetyl iodide gave *A.C.* 58·5%; benzyl chloride gave *A.C.* 66·8%; *epi*chlorohydrin gave *A.C.* 74·3%; ethyl chloroformate gave *A.C.* 8%. $\beta\beta$-Dichloropropane yielded piperidine hydrochloride according to the equation $C_5H_{10}NH + CMe_2Cl_2 = C_5H_{10}NH,HCl + CH_2{:}CMeCl$; tetrachloroethane reacted according to the equation $B + C_2H_2Cl_4 = B,HCl + CHCl{:}CCl_2$; carbonyl chloride yielded the unstable compound, $CO(C_5H_{10}N)_2,2HCl$; acetyl thiocyanate gave nearly pure 1-*acetylpiperidine thiocyanate*, m. p. 83—85°; phenyl-propionyl chloride, benzenesulphonyl chloride, arsenic trichloride, antimony trichloride, chromyl chloride, pentachloroethane, hexa-chloroethane, and carbon tetrachloride yielded only piperidine hydrochloride; *s*-dibromoethane gave piperidine hydrobromide; bromoform yielded *A.C.* 41%; acetyl bromide yielded *A.C.* 72%; and *iso*butyryl bromide gave *A.C.* 86·7%.   J. C. W.

Nitroaminoquinolines. ADOLF KAUFMANN and OTTO ZELLER [with JULES MARTON] (*Ber.*, 1917, **50**, 1626—1630).—The *p*-toluenesulphonyl derivatives of aminoquinolines can very readily be nitrated, and the products are easily hydrolysed to the nitro-amines by means of concentrated sulphuric acid.

5-Aminoquinoline, b. p. 184°/10 mm., m. p. 109—110°, forms a p-*toluenesulphonyl* compound, in stout, white needles, m. p. 203—204°, which reacts with nitric acid (D 1·5) at 60° to give 6 : 8-*dinitro-5-p-toluenesulphonylaminoquinoline*, m. p. 215°.

6-Aminoquinoline, b. p. 187°/11 mm., m. p. 118°, yields a p-*toluenesulphonyl* derivative, glistening, white crystals, m. p. 195°, which reacts with 60% nitric acid at 70° to form 5-*nitro-6-p-toluenesulphonylaminoquinoline*, glistening, yellow crystals, m. p. 168—169°, and this may be hydrolysed to 5-*nitro-6-aminoquinoline*, yellow needles, m. p. 178° (*picrate*, m. p. 270°). The position of the nitro-group follows from the fact that the product of the action of iron and hydrochloric acid, 5 : 6-*diaminoquinoline*, pale brown bundles of needles, m. p. 95°, reacts with phenanthraquinone to form a yellow *azine*, m. p. 287—288°.

8-Aminoquinoline, b. p. 157—162°/20—24 mm., m. p. 65°, yields a p-*toluenesulphonyl* compound, hard, white needles, m. p. 154—156°, which reacts with 60% nitric acid at 50° to form 5 : 7-*dinitro-8-p-toluenesulphonylaminoquinoline*, silky crystals, m. p. 239—240° ·(decomp.), and a small amount of a more soluble *mono-*

nitro-derivative, m. p. 199—200°. These yield Claus's 5:7-dinitro-8-aminoquinoline, m. p. 187—188°, on hydrolysis.

J. C. W.

Phenazoxonium and its Simplest Derivatives. F. KEHRMANN and A. BOUBIS (*Ber.*, 1917, **50**, 1662—1667. Compare A., 1914, i, 868; 1915, i, 586).—As an outcome of the discovery that phenazothionium forms both *meri*- and *holo*-quinonoid salts, it was suggested that a new investigation of the azoxoniums would prove that these are also normal in their behaviour towards acids. The present chemical and optical notices (following abstracts) show that the supposition was well founded.

The reddish-violet salts obtained by dissolving phenazoxine in sulphuric acid, whether dilute or concentrated, are *meri*-quinonoid, mono-acid salts. If hydrogen peroxide is added to the solutions in concentrated sulphuric or perchloric acid, yellow *holo*-quinonoid, di-acid salts are formed. These are unstable, but can be preserved for a short time at 0—10°. On diluting the yellow solutions with glacial acetic acid, the colour changes to wine-red, *holo*-quinonoid, mono-acid salts being formed. The *holo*-quinonoid, *monoperchlorate* (annexed formula), can even be

$C_6H_4 \lll{}^N_O{>} C_6H_4$

ClO_4

isolated as an explosive, brown, glistening powder, but the successful preparation is a matter of chance, as the salt readily changes to the *meri*-quinonoid compound.
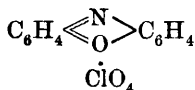
In the case of 3:9-dimethylphenazoxonium, dark red solutions of the *holo*-quinonoid di-acid sulphate may be obtained by dissolving the base in a mixture of the concentrated acid and hydrogen peroxide; on dilution with glacial acetic acid, orange-coloured solutions of the *holo*-quinonoid mono-acid salt result. A brownish-red, *holo*-quinonoid *picrate*, $C_{20}H_{14}O_8N_4$, and a dark violet, *meri*-quinonoid *monoperchlorate* may be isolated as crystalline powders.

5-Aminophenazoxonium yields an explosive, very dark green *holo*-quinonoid *perchlorate*, $NH_2 \cdot C_{12}H_7N \colon O \cdot ClO_4$, which gives a blood-red solution of the *holo*-quinonoid di-acid salt in concentrated sulphuric acid. No tri-acid salt is formed.

3-Aminophenazoxonium perchlorate is a dark red, para-quinonoid salt, and not ortho-quinonoid, thus: $C_{12}H_7ON \colon NH_2 \cdot ClO_4$. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

Quinoneimide Dyes. VII. Spectra of the Simplest Azoxine Dyes. F. KEHRMANN and MAURICE SANDOZ (*Ber.*, 1917, **50**, 1667—1673).—An account, with tables and reproductions of the curves, of the absorption spectra of the salts of phenazoxonium, 3:9-dimethyl-, and 5- and 3-amino-phenazoxoniums (compare preceding abstract).

meri-Quinonoid phenazoxonium salts exhibit a band with maximum at λ 530 $\mu\mu$; the *holo*-quinonoid, di-acid salts give a maximum at 460 $\mu\mu$, and the mono-acid salts show two maxima, the principal one being at 530 $\mu\mu$. For the dimethylphenazoxonium salts, the maxima are: *meri*-quinonoid, 570 $\mu\mu$, and faint bands at 450 $\mu\mu$

and in the extreme violet; *holo*-quinonoid, di-acid salts, 500 $\mu\mu$, and mono-acid salts, 560 $\mu\mu$.

The *holo*-quinonoid, mono-acid salts of 5-aminophenazoxonium give a maximum in the infra-red, whilst the di-acid salts have maxima at 535 $\mu\mu$ and 430 $\mu\mu$; the salts are therefore ortho-quinonoid. The mono-acid salts of 3-aminophenazoxonium have maxima at 492 and 395 $\mu\mu$; the di-acid salts give maxima at 640 and 590 $\mu\mu$, which proves that these salts are para-quinonoid.

In the ultra-violet, all these salts give absorption bands with maxima at 265 and 285 $\mu\mu$. Phenazothionium salts, on the other hand, give one band, at 290 $\mu\mu$. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

Quinoneimide Dyes. VIII. Supplementary Observations on the Absorption Spectra of the Simplest Azothionium Compounds. F. KEHRMANN and M. SANDOZ (*Ber.*, 1917, **50**, 1673—1682. Compare A., 1915, i, 586).—The absorption spectra of the following phenazothionium salts are reproduced by curves and tables: *phenazothionium*: di-acid salts, yellowish-green, maxima in infra-red, at λ 520 $\mu\mu$ and 460 $\mu\mu$; mono-acid salts, blood-red, λ 518 and 435 $\mu\mu$; *6-methylphenazothionium*: di-acid salts, yellowish-green, λ 460 $\mu\mu$ and in infra-red; mono-acid salts, constitution in doubt, blood-red, λ 515 $\mu\mu$ and border of ultra-violet; *5-aminophenazothionium*: di-acid salts, yellowish-blood-red, λ 540 and 440 $\mu\mu$; mono-acid salts, yellowish-green, λ 410 $\mu\mu$ and infra-red.

[With A. BOUBIS.]—5-*Aminophenazothionium perchlorate* (annexed formula) may be obtained in moss-green, slender, explosive needles by

$$\mathrm{NH_2 \cdot C_6H_3} {\ll}^{\mathrm{N}}_{\mathrm{S}}{>} \mathrm{C_6H_4}$$
$$\mathrm{\overset{.}{C}lO_4}$$

oxidising 5-aminothiodiphenylamine with ferric chloride and perchloric acid. It gives solutions of the di-acid salt in concentrated sulphuric acid.

[With G. ROCHAT and A. BOUBIS.]—Thiodiphenylmethylamine is oxidised by means of sodium nitrite in glacial acetic acid to the sulphoxide, which gives a green solution of the di-acid salt of 6-methylphenazothionium in 70% perchloric acid. [See also *J. Soc. Chem. Ind.*, 1918, 119A.] J. C. W.

Quinoneimide Dyes. IX. Absorption Spectra of the Mono-acid Salts of Phenyl Derivatives of 3 : 9-Diaminophen-azoxonium. F. KEHRMANN and M. SANDOZ (*Ber.*, 1917, **50**, 1682—1683).—The tables referred to in the preceding abstract also contain the following data: 3 : 9-*diaminophenazoxonium monohydrochloride*, solutions in alcohol, bluish-violet, λ 593, 570, 545 $\mu\mu$; 3-*amino-9-anilinophenazoxonium* (9)-*hydrochloride*, blue, λ 605 $\mu\mu$; 3 : 9-*dianilinophenazoxonium monohydrochloride*, greenish-blue, λ 664 $\mu\mu$; 3 : 9-*tetramethyldiaminophenazoxonium nitrite*, greenish-blue, λ 645, 588 $\mu\mu$; and 3-*dimethylamino-9-anilinophenaz-oxonium* (9)-*monohydrochloride*, greenish-blue, λ 651 $\mu\mu$.

The fact is again emphasised that all the phenazothioniums

behave alike in the ultra-violet spectrum, exhibiting an absorption band at $\lambda\,290\,\mu\mu$, whilst the phenazoxoniums are all alike in giving two maxima, $\lambda\,265$ and $285\,\mu\mu$. [See also *J. Soc. Chem. Ind.*, 1918, 119a.] J. C. W.

Steric Hindrance. III. J. von Braun and M. Mintz (*Ber.*, 1917, **50**, 1651—1656. Compare A., 1913, i, 1333; 1916, i, 647). —In the first paper of this series, on tetramethyldiaminodiaryl-methanes, it was shown that if both basic groups are encumbered by hindering neighbours, the compounds do not react at all readily with cyanogen bromide or iodoacetonitrile, but if only one group is sterically hindered, then reactions can take place at both tertiary amino-groups. Another example is now given; the compound (I) is inactive, but the base (II) reacts at both nitrogen atoms.

(I.)   (II.)
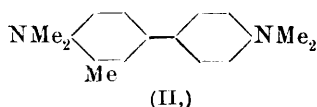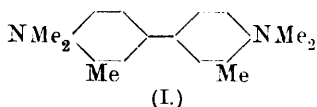
Tetramethyl-*o*-tolidine (I), prepared by heating *o*-tolidine with methyl iodide and sodium carbonate solution, reacts sluggishly with iodoacetonitrile to form *dimethyldicyanomethyl-o-tolidine*,
$$CN \cdot CH_2 \cdot NMe \cdot C_6H_3Me \cdot C_6H_3Me \cdot NMe \cdot CH_2 \cdot CN,$$
m. p. 163°.
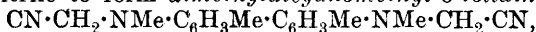
3-Methylbenzidine, from the reduction of *o*-methylazobenzene, forms a glassy mass, b. p. 225°/4 mm., and yields a *picrate*, m. p. 204°. If this is methylated by the above method, it gives the *methiodide*, $NMe_2 \cdot C_6H_3Me \cdot C_6H_4 \cdot NMe_3I$, m. p. 155—156°, which is converted by heating at 180—200°/4 mm. into *tetramethyl-3-methylbenzidine* (II), m. p. indefinite, 63—70°. This base forms a *picrate*, m. p. 193°, and a 6 : 6'-*dinitro*-compound, m. p. 110°, and reacts with cyanogen bromide to give *dicyanodimethyl-3-methylbenzidine*, $CN \cdot NMe \cdot C_6H_4 \cdot C_6H_3Me \cdot NMe \cdot CN$, m. p. 138—139°, which may be hydrolysed to the oily *dimethyl-3-methyl-benzidine*, this yielding a *dinitroso*-derivative, m. p. 195°. When the tertiary base (II) is warmed with iodoacetonitrile, three products are formed, one being insoluble in hot water, another insoluble in cold water, and the third very soluble. The first is *dimethyldicyanomethyl-3-methylbenzidine*, m. p. 93—94°; the second is a quaternary *iodide* of the formula
$$CN \cdot CH_2 \cdot NMe \cdot C_6H_3Me \cdot C_6H_4 \cdot NMe_3I,$$
m. p. 145—148°; and the third is the diquaternary *di-iodide* of the original base, $I \cdot NMe_3 \cdot C_6H_4 \cdot C_6H_3Me \cdot NMe_3I$, m. p. 155°. J. C. W.
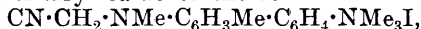
Nitro-derivatives of *iso*Oxadiazole Oxides and of *iso*Oxa-diazoles. Arthur G. Green and Frederick Maurice Rowe (T., 1918, **113**, 67—74. Compare T., 1913, **103**, 2025).—Attention has already been directed to the acidic nature of 4 : 6-dinitrobenz-*iso*oxadiazole oxide. This acidity is either to be attributed to the

hydrogen atom at position 5, or possibly the compound is really 4 : 6-dinitro-5-hydroxybenz*iso*oxadiazole, thus:

$$NO_2 \quad N \qquad\qquad NO_2$$

(I.)   or   (II.)

A compound of the formula (I) would require 20 atoms of hydrogen per molecule for reduction, whilst a substance of the alternate type (II) would absorb 18 atoms. As a matter of fact, it is found on titration with titanous chloride that 20 atoms are used.

Nitro-derivatives of naphth*iso*oxadiazole and its oxide (A., 1917, i, 518) have been prepared. They probably have the formulæ

$$\text{and (4, and 5) } NO_2 \cdot C_{10}H_5 <^N_N> O$$

For experimental details, see the original.   J. C. W.

Mechanism of the Coupling Reaction. OTTO DIMROTH, HELMUT LEICHTLIN, and OTTO FRIEDEMANN (*Ber.*, 1917, **50**, 1534—1548).—The first stage in the coupling of a diazonium salt with a phenol was supposed by Dimroth to consist in the formation of a diazo-ether, which would subsequently undergo rearrangement into the ordinary azo-compound. It was found, for example, that *p*-nitrophenol and *p*-bromobenzene-diazonium chloride gave an unstable intermediate compound of the constitution $NO_2 \cdot C_6H_4 \cdot O \cdot N_2 \cdot C_6H_4Br$, which changed into the normal compound, $NO_2 \cdot C_6H_3(OH) \cdot N_2 \cdot C_6H_4Br$ (A., 1907, i, 662). Two criticisms of this theory have appeared. One is based on the fact that phenolic ethers also form azo-compounds, which has led to the view that addition of the diazonium compound takes place at the conjugated double linkings (Meyer and others, A., 1914, i, 882). On the other hand, Auwers has suggested that the first products are not ethers, $R \cdot O \cdot N \colon N \cdot R'$, but diazonium salts, $R \cdot O \cdot NR' \colon N$ (A., 1915, i, 85). An answer to the second criticism is now given.

Morgan and Wootton's stable diazonium salts, 4-benzoylamino-naphthalene-1-diazonium chloride and *p*-acetylaminobenzene-diazonium chloride, have been treated with phenols ranging in strength from picric acid to pentamethylphenol. The molecular conductivities of the products in 80% acetone at 0° have been measured, and the results show that the compounds with picric acid and dinitrophenol are true diazonium salts with the same conductivities as the chlorides or trichloroacetates, whereas the weaker phenols and enols give true ethers with conductivities as low as that of *p*-nitrobenzeneazomethyl ether.

Benzoyl-1 : 4-naphthalenediamine is obtained from the 4-nitro-

compound by a slight modification of Morgan's method (T., 1907, **91**, 1316) and converted into the diazonium chloride. This reacts with dilute sodium hydroxide to form, not the nitrosoamine, $NHBz \cdot C_{10}H_6 \cdot NH \cdot NO$, as Morgan supposed, but the *quinonediazide*,

$NBz{:}C_{10}H_6{<}^{N}_{N}$, which crystallises from diluted acetone as a

brownish-yellow substance. *4-Benzoylaminonaphthalene-1-diazonium trichloroacetate*, m. p. 124° (decomp.), *picrate*, m. p. 141—142°, and 2:4-*dinitrophenoxide*, m. p. 75° (decomp.), are prepared by precipitation from the chloride and the acid or phenol, with or without the addition of sodium acetate. The diazonium chloride couples with *p*-nitrophenol to form *4-benzoylaminonaphthalene-1-azo-p-nitrophenyl ether*,

$$NHBz \cdot C_{10}H_6 \cdot N{:}N \cdot O \cdot C_6H_4 \cdot NO_2,$$
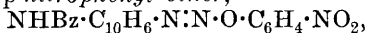
m. p. 115—120° (decomp.), which has a somewhat higher conductivity than the other diazo-ethers. The enolic form of dibenzoylacetylmethane yields *4-benzoylaminonaphthalene-1-azo-αα-dibenzoyl-β-Δ^α-propenyl ether*, $NHBz \cdot C_{10}H_6 \cdot N{:}N \cdot O \cdot CMe{:}CBz_2$, m. p. 134—135°; this is completely hydrolysed by ethereal hydrochloric acid only after some hours, the components being formed on the one hand, and acetyl chloride and the *compound*,

$$NHBz \cdot C_{10}H_6 \cdot NH \cdot N{:}CBz_2,$$
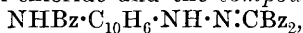
brownish-yellow crystals, m. p. 225°, on the other. *p-Acetylaminobenzeneazo-αα-dibenzoyl-β-Δ^α-propenyl ether* forms large, yellow crystals, m. p. 145—146°.

For the preparation of pentamethylphenol, *s.-m*-xylidine hydrochloride is heated with methyl alcohol at 250°, and the pentamethylaniline is diazotised. Pentamethylphenol is so feebly acidic that the alternative quinonoid formula has to be considered, thus : $H \cdot C_6Me_5{:}O \longrightarrow C_6Me_5 \cdot OH$. It dissolves more freely in alkalis than in water (1 litre of boiling water dissolves 1·5 grams; 1 litre of boiling 0·8N-potassium hydroxide dissolves 12 grams), but the free phenol, and not the salt, crystallises from saturated solutions. Furthermore, the conductivity of a mixture of the phenol and sodium hydroxide in 50% alcohol does not vary with time. The phenol is therefore not an enolisable ketone, but a true, but very weak, hydroxy-compound, comparable with amyl alcohol.

Benzeneazo pentamethylphenyl ether, $C_6Me_5 \cdot O \cdot N{:}NPh$, is a very unstable, brownish-yellow substance, which may even explode spontaneously at the ordinary temperature. *4-Benzoylaminonaphthalene-1-azo pentamethylphenyl ether* is quite harmless to handle, but the pale yellow granules explode at 81°. *p-Acetylaminobenzeneazo pentamethylphenyl ether* is a straw-yellow powder which detonates at 69°.

Mesitol and *iso*durenol also give precipitates of diazo-ethers when mixed with neutralised diazonium salt solutions of the above types, but the products decompose before they can be dried. [See also *J. Soc. Chem. Ind.*, 1918, 118A.]   J. C. W.

Swelling of Fibrin in Polybasic Acids and their Salts. MARTIN H. FISCHER and MARTIN BENZINGER (*J. Amer. Chem. Soc.*, 1918, **40**, 292—303).—Experiments on the absorption of

water by fibrin in acid and alkaline solutions containing the acid
salts (using phosphoric and citric acids) gave essentially the same
results as when gelatin was used (see below), with the exception
that the points of minimum absorption corresponded with a
different acid content in the solution. [See also *J. Soc. Chem.
Ind.*, 1918, 131A.]   L. A. C.

Preparation of Plant Nucleic Acids. GEORGE CLARKE and
SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1917, **11**, 319—324).—
Nucleic acid is extracted from plant tissues by 10% sodium chloride
solution in the form of nucleates of proteins, and is precipitated
in this form from the extract by hydrochloric acid. If the plant
material is first boiled with strong alcohol, subsequent extraction
with salt solution and precipitation with acid yields a product free
from proteins. Methods for the preparation of nucleic acid from
yeast and from wheat embryos are described. The purified pro-
ducts from both sources contain the proportions of nitrogen and
phosphorus required by Levene's formula, $C_{38}H_{50}O_{29}N_{15}P_4$ (A.,
1909, i, 541). [See also *J. Soc. Chem. Ind.*, 1918, March.]
                                                      J. H. L.

**Structure of Yeast-nucleic Acid. II. Uridinephosphoric
Acid.** P. A. LEVENE (*J. Biol. Chem.*, 1918, **33**, 229—234. Compare
Levene, A., 1917, i, 670).—The previously described cytosine–
uracil–dinucleotide is now shown to be a mixture of the two simple
mononucleotides, the brucine salts of which can be separated by
fractional crystallisation from 35% alcohol. The less soluble frac-
tion consists of *brucine uridinephosphate*, $C_{55}H_{63}O_7N_6P,7H_2O$,
which contracts at 183°, then melts, and finally decomposes at 198°
(corr.). It is converted into the *barium* salt, $C_9H_{11}O_9N_2PBa$, crystal-
lising from water in rosettes of long needles, $[\alpha]_D^{20} + 3\cdot5°$, in a
2·5% solution of hydrochloric acid. After hydrolysis, the only
pyrimidine which can be detected is uracil.

The more soluble fraction consists of *brucine cytidinephosphate*,
but the corresponding barium salt has not yet been obtained in a
crystalline form. In the light of these results, the presence of a
tetraribose nucleus in yeast-nucleic acid (see Jones and Read, A.,
1917, i, 233) cannot yet be regarded as established.   H. W. B.

Swelling of Gelatin in Polybasic Acids and their Salts.
MARTIN H. FISCHER and MARIAN O. HOOKER (*J. Amer. Chem.
Soc.*, 1918, **40**, 272—292).—The absorption of water by gelatin
was determined in different concentrations of the primary, binary,
and ternary salts of phosphoric, citric, and carbonic acids, and in
solutions varying from pure acid to pure alkali (sodium hydroxide)
for the same three acids. The absorption is greatest in pure acids
and alkali, decreasing considerably in the presence of salts, and
with certain salts at high concentrations is less than in pure water.
From a certain minimum there is a progressive increase in the
absorption with increase of the acid or alkali content of the mix-
ture. The results are held to be applicable to absorption by proto-

plasm in living cells, there being increased turgor or œdema with every increase in the acid or alkali content of the cell, even in the presence of "buffer" salts. [See also *J. Soc. Chem. Ind.*, 1918, 131A.]   L. A. C.

The Liquefaction or "Solution" of Gelatin in Polybasic Acids and their Salts.

MARTIN H. FISCHER and WARD D. COFFMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 303—312).—Experiments showed that there is a progressive increase in the tendency of gelatin to go into solution in mixtures of the salts of polybasic acids as the amount of acid or alkali in these mixtures is increased from a given low point. This shows that hydration and "solution" of a protein are not the same thing, for if they were, the addition of an acid or an alkali to a solution should cause it to gel, for this causes increased hydration (see previous abstracts). The results have an important bearing on many physiological problems, such as acid intoxication, digestion, etc. [See also *J. Soc. Chem. Ind.*, 1918, 131A.]   L. A. C.

Chemical Composition and Biological Availability of Peptone.

L. DAVIS (*J. Lab. Clin. Med. St. Louis*, 1917, **3**, 75—86; from *Physiol. Abstr.*, 1918, **2**, 662).—A comparison of domestic peptones with Witte's product. It is most important to determine the products of hydrolysis, physical properties and elementary chemical analysis being secondary to this. Tyrosine and tryptophan are important constituents. The best comparison is given by quantitative biochemical tests, such as the elaboration of diphtheria and tetanus toxins and the production of indole. Domestic peptones do not give a potent diphtheria toxin, although furnishing good tetanus toxin and frequently yielding indole.

W. G.

The Surface Tension of Solutions of Ferments.

L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 50—58).—Stalagmometric measurements of solutions of various enzymes.   S. B. S.

The "Reversion of Diastatic Action."

L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 37—41).—The amount of starch precipitated when its solutions are treated with diastase depends on their previous treatment. If soluble starch solutions of varying concentrations are treated with the same amount of diastase, it will be found that within a given time starch precipitation will appear first in lower concentrations of those solutions which have been cooled before being submitted to the ferment (at the ordinary temperature), and in higher concentrations of solutions which have been heated. The action of the diastase is ascribed by the author to the aggregation of colloidal particles. The action of diastase diminishes the viscosity, and thus promotes the precipitation of the larger particles as they are formed. The cooled solution of starch will, before treatment with diastase, contain more of the larger

h 2

aggregates than the heated solution.   [See also *J. Soc. Chem. Ind.*, 1918, 133a.]   S. B. S.

Action of Oxidising and Reducing Substances on Diastases.

L. BERCZELLER and E. FODOR (*Biochem. Zeitsch.*, 1917, **84**, 42—49). —Potassium permanganate, hydrogen peroxide, and iodine in very small concentrations inhibit the action of diastase.   Ordinary formaldehyde ("formalin") accelerates slightly the diastatic action, but this acceleration is due to the formic acid it contains.   If neutralised, it has a slight inhibitory action.   S. B. S.

Enzyme Action. XVI. Formation of Ester-hydrolysing Substances by the Action of Alkali on Proteins.

FLORENCE HULTON-FRANKEL (*J. Biol. Chem.*, 1917, **32**, 395—407.   Compare Falk, A., 1917, i, 598).—Proteins (caseinogen, gelatin, etc.) are shaken with alkali solutions, and after twenty-four hours the turbid liquids are treated with hydrochloric acid until only a slightly alkaline reaction is obtained.   Portions then incubated with ethyl butyrate or other esters cause a distinctly greater hydrolysis to occur than is observed in control solutions of the same hydroxyl-ion concentration.   The most active solutions are obtained when the concentration of the alkali acting on the protein is about $3N$. Raising the temperature to 80° increases the activity of the result-ing lipolytic solution.   When treated with acid instead of alkali, the protein solutions are devoid of ester-hydrolysing properties. Dialysis only partly removes the lipolytic property of the alkali-protein solutions, whilst boiling does not exert the slightest in-activating action.   [See, further, *J. Soc. Chem. Ind.*, 1918, 135a.]
                                                                 H. W. B.

The Preparation of Urease from Bacteria.

MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **84**, 354—357).—The bacteria are removed from the culture on agar and dried on porous porcelain. A preparation is thus obtained which can be preserved for a long time, and is active in the presence of toluene.   S. B. S.

The Formation of Ferments. V.

MARTIN JACOBY (*Biochem. Zeitsch.*, 1917, **84**, 358).—The addition of leucine does not increase the activity of the permanent urease preparation (see preceding abstract), but rather inhibits it.   This fact indicates, taken in conjunction with the author's previous work, that this amino-acid is necessary for the formation of the enzyme, but has no effect on its activity.   S. B. S.

Silicon-Hydrocarbons with Nuclei containing Halogens, and their Use in Syntheses.

GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 1559—1568).—*p*-Chlorobromo- and *p*-dibromo-benzene react with magnesium to form the magnesium *p*-halogenophenyl bromides.   When these are treated with silicon tetrachloride, they yield the trichloro-*p*-halogenophenylmonosilanes, $SiCl_3 C_6H_4X$, which react with magnesium alkyl haloids to form *p*-halogenophenyltrialkylmonosilanes.   Compounds of this type

react most readily with magnesium, but not very smoothly with sodium, but they may be applied very extensively in Grignard and Fittig syntheses. Some very unusual examples are now described.

Magnesium p-bromophenyl bromide and silicon tetrachloride yield *trichloro-p-bromophenylmonosilane* (p-*bromophenylsilicon trichloride*), a colourless oil, b. p. 120—125°/15 mm., which is immediately hydrolysed by water to p-*bromophenylsilicic acid* ("*hydroxyoxo-p-bromophenylmonosilane*," according to Stock's nomenclature), $C_6H_4Br \cdot SiO \cdot OH$, a white powder, and also *dichlorodi-p-bromophenylmonosilane*, $SiCl_2(C_6H_4Br)_2$, snow-white prisms, m. p. 60°, b. p. 238—240°/21 mm. The trichloride reacts with magnesium ethyl bromide to form p-*bromophenyltriethylmonosilane*,

$$SiEt_3 \cdot C_6H_4Br,$$
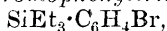
b. p. 149°/14 mm., D_4^{21} 1·1643 n_{H_a} 1·52836, n_D 1·53280, $n_{H\beta}$ 1·54411, n_{H_γ} 1·55395, at 21°.

From p-chlorobromobenzene, the following compounds may be obtained by the same reactions. *Trichloro-p-chlorophenylmonosilane*, b. p. 105°/15 mm.; p-*chlorophenylsilicic acid*, a colourless powder; p-*chlorophenyltriethylmonosilane*, b. p. 261—262°/760 mm., 137°/14·5 mm., $D_4^{9\cdot6}$ 1·0056, n_{H_a} 1·51777, n_D 1·52193, $n_{H\beta}$ 1·53255, n_{H_γ} 1·54168, at 9·6°; p-*chlorophenyltri-*n-*propylmonosilane*, b. p. 160°/14 mm., D_4^9 0·9708, n_{H_a} 1·50835, n_D 1·51234, $n_{H\beta}$ 1·52225, n_{H_γ} 1·53059, at 9°.

p-Bromophenyltriethylmonosilane reacts readily with magnesium that has been etched by iodine to give the organo-magnesium compound in about 90% yield. This is ascertained from the weight of phenyltriethylmonosilane, b. p. 230—240°, left on decomposing the compound with water. The following products have been obtained from the magnesium compound: by means of iodine, p-*iodophenyltriethylmonosilane*, a colourless liquid, b. p. 165°/13 mm., D_4^{20} 1·3304, n_{H_γ} 1·55711, n_D 1·56233, $n_{H\beta}$ 1·57578, n_{H_γ} 1·58709, at 20°; with lead trimethyl bromide, p-*triethylsilyltrimethylplumbylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot PbMe_3$, a stable, viscous oil, b. p. 191°/17 mm., D_4^{23} 1·3997, n_{H_a} 1·54379, n_D 1·54937, $n_{H\beta}$ 1·56240, n_{H_γ} 1·57417, at 23·8°, which is resolved by bromine at $-75°$ into lead trimethyl bromide and p-bromophenyltriethylmonosilane; by means of tin triethyl bromide, p-*triethylsilyltriethylstannylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot SnEt_3$, a colourless, viscous oil, b. p. 214°/18 mm., $D_4^{21\cdot2}$ 1·1216, n_{H_a} 1·52316, n_D 1·52756, n_β 1·53888, n_{H_γ} 1·54864, at 21·2°.

p-Chlorophenyltriethylmonosilane reacts with chlorodiphenylarsine in the presence of sodium to form p-*diphenylarsyltriethylsilylbenzene*, $SiEt_3 \cdot C_6H_4 \cdot AsPh_2$, as a colourless, viscous oil, b. p. 279—281°/17 mm., $D_4^{21\cdot3}$ 1·1661, n_{H_γ} 1·60784, n_D 1·61455, $n_{H\beta}$ 1·63181, n_{H_γ} 1·64718, at 21·3°, which forms crystalline *additive* compounds with mercuric salts (*chloride*, m. p. 188°; *bromide*, m. p. 181°; *iodide*, m. p. 139·5°).

From the optical data, the molecular refractions and dispersions of the above p-halogenophenyltrialkylmonosilanes have been calculated, and the atomic refractions and dispersions of the silicon atom have been worked out. These are tabulated with Bygdén's

values for phenyltriethylmonosilane (A., 1915, ii, 809), and it is obvious that the contribution of the silicon atom rises with the mass of the groups attached to it.

All densities are reduced to vacuum standard.   J. C. W.

Benzyltrimethylsilicane-p-sulphonic Acid and some of its Derivatives. ARTHUR BYGDÉN ($J.$ $pr.$ $Chem.$, 1917, [ii], **96,** 86—104).

—Benzyltrimethylsilicane (Bygdén, A., 1912, i, 341) can be fairly easily converted into a sulphonic acid which, unlike most of the organic silicane sulphonic acids described previously, is easily isolated and convertible into crystalline salts.

When treated in chloroform solution with an equimolecular quantity of chlorosulphonic acid, benzyltrimethylsilicane yields *benzyltrimethylsilicane*-p-*sulphonic acid,* $SiMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_3H$, rectangular tablets with $2H_2O$, which melt in their water of crystallisation at 99—114°; the monohydrated acid has m. p. 116·0—116·5°; the position of the sulphonic acid group is demonstrated by the formation of p-hydroxybenzoic acid on fusing with potassium hydroxide and of toluene-p-sulphonic acid on boiling with aqueous potassium hydroxide. The following salts were prepared: *potassium* salt, rectangular or rhombic leaflets with $1H_2O$; *rubidium* salt, rectangular leaflets with $1H_2O$; *caesium* salt, hexagonal leaflets with $\frac{1}{2}H_2O$; *sodium* salt, leaflets with $2H_2O$; *lithium* salt, crystals with $2H_2O$; *calcium* salt, rhombic tablets with $2H_2O$; *strontium* salt, needles with $2H_2O$; *barium* salt, needles with $2H_2O$; *magnesium* salt, rhombic leaflets with $7\frac{1}{2}H_2O$; *zinc* salt, platelets or needles with $6H_2O$; *cadmium* salt, platelets or needles with $6H_2O$; *ferrous* salt, almost colourless leaflets with $7H_2O$; *nickel* salt, green leaflets or needles with $7H_2O$; *cobalt* salt, red leaflets with $8H_2O$; *lead* salt, needles with $2H_2O$; *copper* salt, blue leaflets with $6H_2O$; *silver* salt, rectangular leaflets with $2H_2O$; *ammonium* salt, tablets with $1H_2O$; *methylammonium* salt, elongated tablets, m. p. 144—172°; *ethylammonium* salt, leaflets, prisms, or tablets, m. p. 110·5—111·5° (corr.); *brucine* salt, rhombic tablets, m. p. 215·5—217·5° (corr.). The potassium salt of the sulphonic acid on treatment with phosphorus pentachloride yielded *benzyltrimethylsilicane*-p-*sulphonyl chloride,*

$$SiMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_2Cl,$$
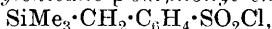
tablets, m. p. 45·5—46·5° (corr.), and the corresponding *bromide,* $SiMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_2Br$, rectangular tablets, m. p. 60—60·5° (corr.), was obtained in a similar manner with the use of phosphorus pentabromide. By allowing the acid chloride to react in ethereal solution with various bases, *benzyltrimethylsilicane*-p-*sulphonamide*, $SiMe_3 \cdot CH_2 \cdot C_6H_4 \cdot SO_2 \cdot NH_2$, tablets or prisms, m. p. 81—81·5° (corr.), and the corresponding *methylamide*, prisms, m. p. 76·4—77·2° (corr.), *benzylamide*, leaflets, m. p. 130·5—131° (corr.), *anilide*, hexagonal or rhombic tablets, m. p. 124·2—125° (corr.), *methylanilide*, needles, m. p. 71·5—72·5° (corr.), o-*toluidide*, tablets, m. p. 153—153·5° (corr.). and p-*toluidide*, rhombic tablets, m. p. 97—98° (corr.), were also prepared.   D. F. T.

New Heterocyclic Systems. IV. Dimethyl- and Diethyl-*cyclo*pentamethylenestannine and their Scission Products. GERHARD GRÜTTNER, ERICH KRAUSE, and MAXIMILIAN WIERNIK (*Ber.*, 1917, **50**, 1549—1558. Compare A., 1917, i, 122).—Cyclic compounds containing five carbon atoms and one tin atom in the ring have now been obtained by methods analogous to those employed in the case of lead.

Tin diethyl dibromide, which is readily prepared by heating tin filings with ethyl bromide at 175—180°, reacts with the magnesium compound of αε-dichloropentane to form *diethyl*cyclopentamethylene-stannine, $C_5H_{10}{:}SnEt_2$, which is a colourless, mobile oil, with the odour of fir-needle extract, and has b. p. 95°/14 mm., $D_4^{19\cdot9}$ 1·2693, $n_{H\alpha}$ 1·50298, n_D 1·50673, $n_{H\beta}$ 1·51586, $n_{H\gamma}$ 1·52357, at 19·9°. The oil is stable in the absence of air, but otherwise it gradually deposits a white resin. The ring is opened by means of bromine, diluted with ethyl acetate, at 0°, when *tin diethyl-ε-bromoamyl bromide*,

$$C_5H_{10}Br{\cdot}SnEt_2Br,$$
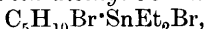
is formed as a very viscous oil, b. p. 190·5°/16 mm., D_4^{20} 1·7113, $n_{H\alpha}$ 1·54270, n_D 1·54707, $n_{H\beta}$ 1·55768, $n_{H\gamma}$ 1·56675, at 20·3°. This reacts with magnesium ethyl bromide to form *tin triethyl-ε-bromoamyl*,

$$SnEt_3{\cdot}C_5H_{10}Br,$$
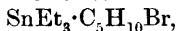
which is a stable, almost odourless, mobile oil, b. p. 155·5°/15 mm., D_4^{20} 1·3723, $n_{H\alpha}$ 1·50204, n_D 1·50563, $n_{H\beta}$ 1·51457, $n_{H\gamma}$ 1·52213, at 19·1°. The halogen is removed from this substance by converting it into its magnesium compound and decomposing this with water; the main product is *tin triethyl-n-amyl*, b. p. 110°/15 mm., D_4^{20} 1·1258, $n_{H\alpha}$ 1·47070, n_D 1·47400, $n_{H\beta}$ 1·48216, $n_{H\gamma}$ 1·48904, at 20°, but there is formed as well some *ακ-hexaethyldistannyldecane*,

$$SnEt_3{\cdot}[CH_2]_{10}{\cdot}SnEt_3,$$
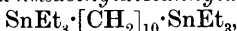
which distils without decomposition, and has b. p. 248°/15 mm., $D_4^{20\cdot7}$ 1·1887, $n_{H\alpha}$ 1·49480, n_D 1·49835, $n_{H\beta}$ 1·50637, $n_{H\gamma}$ 1·51421, at 20·7°. *Tin diethyl-n-amyl bromide*, $C_5H_{11}{\cdot}SnEt_2Br$, an unpleasant-smelling, viscous oil, b. p. 135°/15 mm., $D_4^{22\cdot3}$ 1·4365, $n_{H\alpha}$ 1·50484, n_D 1·50866, $n_{H\beta}$ 1·51825, $n_{H\gamma}$ 1·52657, at 22·3°, is formed by the action of bromine on the tin tetra-alkyl.

*Dimethyl*cyclopentamethylenestannine is obtained from tin dimethyl di-iodide, as above; it closely resembles the homologue, and has b. p. 64°/16 mm., $D_4^{23\cdot1}$ 1·3357, $n_{H\alpha}$ 1·49861, n_D 1·50242, $n_{H\beta}$ 1·51184, $n_{H\gamma}$ 1·51993, at 23·1°. *Tin dimethyl-ε-bromoamyl bromide* has b. p. 168°/14·5 mm., D_4^{25} 1·8385, $n_{H\alpha}$ 1·54548, n_D 1·54983, $n_{H\beta}$ 1·56085, $n_{H\gamma}$ 1·57019, at 24°, and *tin trimethyl-ε-bromoamyl* has b. p. 124°/18 mm., $D_4^{23\cdot4}$ 1·4659, $n_{H\alpha}$ 1·49604, n_D 1·49976, $n_{H\beta}$ 1·50895, $n_{H\gamma}$ 1·51677, at 23·4°. The magnesium compound of the latter reacts with lead trimethyl bromide to form *α-trimethylstannyl-ε-trimethylplumbyl-pentane*, $SnMe_3{\cdot}[CH_2]_5{\cdot}PbMe_3$, as a colourless, viscous oil, b. p. 162°/17·5 mm., $D_4^{23\cdot2}$ 1·6482, $n_{H\alpha}$ 1·51822, n_D 1·52282, $n_{H\beta}$ 1·53452, $n_{H\gamma}$ 1·54473, at 23·2°.

Tin triethyl bromide reacts with the magnesium compound of αε-di-chloropentane to form *αε-hexaethyldistannylpentane*, b. p. 205·5°/14·5 mm., D_4^{20} 1·2654, n_D^{20} 1·5053, $n_F - n_C$ 0·01312.

Similarly, lead trimethyl bromide gives *αε-hexamethyldiplumbyl*

pentane, $PbMe \cdot [CH_2]_5 \cdot PbMe_3$, b. p. $166 \cdot 5°/14$ mm., $D_4^{23 \cdot 5}$ $1 \cdot 9448$, $n_D^{23 \cdot 5}$ $1 \cdot 5571$, $n_F - n_C$ $0 \cdot 01940$.

All the densities are reduced to vacuum standard, and in many cases sets of refractive indices at higher temperatures are recorded

J. C. W.

Physiological Chemistry.

Applications of Gas Analysis. III. Apparatus for the Study of the Respiratory Exchange in Small Animals. A. L. PRINCE (*J. Biol. Chem.*, 1917, **32**, 333—336).—The apparatus described is suitable for the study of the respiratory exchange in rats and similar animals and for teaching purposes.   H. W. B.

Applications of Gas Analysis. VI. Respiratory Exchange and Indirect Calorimetry. YANDELL HENDERSON (*J. Biol. Chem.*, 1918, **33**, 47—53).—A simple spirometer is described which permits the measurement of the expired air and the analysis of a sample of it by the methods previously detailed (see this vol., ii, 81). Directions for the calculation of the respiratory quotient and exchange are appended.   H. W. B.

Applications of Gas Analysis. II. Carbon Dioxide Tension of the Venous Blood and the Circulation Rate. YANDELL HENDERSON and A. L. PRINCE (*J. Biol. Chem.*, 1917, **32**, 325—331. Compare A., 1917, ii, 506).—The authors describe a simple method for estimating the carbon dioxide tension of venous blood. The subject makes the deepest possible expiration into an empty rubber bag. After a few minutes, the expired air is inhaled, and after being retained for ten seconds in the lungs is again expired into the bag. This procedure is repeated at intervals five or six times, and then the estimation of the percentage of carbon dioxide gives the required carbon dioxide tension of the venous blood of the patient.   H. W. B.

Relationship between Cholesterol and Cholesterol Esters in the Blood during Fat Absorption. ARTHUR KNUDSON (*J. Biol. Chem.*, 1917, **32**, 337—346. Compare Bloor, A., 1916, i, 450; Bloor and Knudson, A., 1917, i, 236).—During fat absorption in dogs, the cholesterol in the blood remains unchanged, but the amount of cholesterol esters in both plasma and corpuscles increases, the increase being most marked in the corpuscles. Similar changes are observed in the lecithin and total fatty acids of the plasma and corpuscles; indeed, a fairly constant relationship between lecithin, cholesterol esters, and total fatty acids in the blood is noted. The blood corpuscles evidently play a very important part in fat metabolism.   H. W. B.

The Amount and the Distribution of Creatine and Creatinine in Normal Human Blood. ANDREW HUNTER and WALTER R. CAMPBELL (*J. Biol. Chem.*, 1918, **33**, 169—191).—The amount of creatinine in normal human blood plasma ranges under different conditions from 0·7 to 1·3 mg. per 100 c.c., average 1 mg., and it is practically certain that it is distributed through corpuscles and plasma in uniform concentration. It is apt to be lower in the female than in the male, and lower in sedentary than in active subjects.

Creatine is chiefly concentrated in the corpuscles; roughly, it may be said that corpuscles contain 6 to 9 mg. per 100 c.c., whilst plasma contains but 0·4 to 0·6 mg. The blood as a whole seems, on an average, to contain about 3 mg. per 100 c.c. There seems to be more in the blood of females than in that of males.

There is a distinct correspondence between increase of plasma creatine and the appearance of creatine in the urine. A. J. G.

Amino-nitrogen and Dextrose in Lymph and Blood before and after the Injection of Nutrient Solutions in the Intestine. BYRON M. HENDRIX and JOSHUA E. SWEET (*J. Biol. Chem.*, 1917, **32**, 299—307).—In a fasting dog, the thoracic lymph contains less amino-nitrogen but more dextrose than the blood. After the injection of milk, peptone, or amino-acid solutions into the intestine, the amino-nitrogen in both the blood and the lymph increases, but the amount in the lymph is greater than in the blood. The introduction of sugar solutions into the intestine is followed similarly by a large increase in the dextrose content of the lymph and a smaller rise of the dextrose in the blood of the general circulation. In some cases the dextrose in the lymph approximates in amount to that present in the mesenteric veins. The authors suggest that absorption of dextrose and amino-acids takes place into both lymph and blood, but as the volume and rate of flow of the blood are so much greater than those of the lymph, the concentration of dextrose and amino-acid attained in the former is correspondingly less than in the latter fluid. H. W. B.

Use of Indicators for the Colorimetric Determination of the Hydrogen-ion Concentration of Sera. ANNIE HOMER (*Biochem. J.*, 1917, **11**, 283—291).—Six out of fifteen indicators examined can be applied to the colorimetric determination of hydrion concentration in sera, using the Walpole colorimeter. Neutral red gives accurate results over the range $p_H = 5\cdot9$—$7\cdot6$, whilst dibromo-*o*-cresolsulphonephthalein is satisfactory for $p_H = 5\cdot2$—$5\cdot4$, and tetrabromophenolsulphonephthalein for $p_H = 3\cdot0$. *α*-Naphtholphthalein, phenolsulphonephthalein, and dibromothymolsulphonephthalein, the respective ranges of which are $p_H = 7\cdot6$—$8\cdot5$, $6\cdot8$—$8\cdot4$, and $6\cdot0$—$7\cdot6$ in pure solutions, indicate consistently low values of p_H (that is, high acidities) when used with sera, but as the differences are fairly constant for sera containing 4—10% of protein, and as a rule do not exceed one unit, these indicators can be employed in routine work if suitable correc-

tions are made. Each operator should determine the necessary corrections by making comparative determinations of p_H on the same sera colorimetrically and electrometrically. By the colorimetric method, it is possible to determine rapidly the amount of acid or alkali required to adjust the reaction of a serum to any given value within the useful range of any of the indicators mentioned, and also, by interpolation, to certain intermediate values not amenable to direct colorimetric observation.   J. H. L.

Influence of the Heat Denaturation of ψ-Globulin and Albumin on the Nature of the Protein appearing in Concentrated Sera. ANNIE HOMER (*Biochem. J.*, 1917, **11**, 292—306). —The extent of the denaturation of the proteins in antitoxic sera at 57·5° (compare A., 1916, i, 614; 1917, i, 497), as measured by their increased precipitability by ammonium sulphate at 30% of saturation, attains its maximum after four hours' heating when the reaction of the liquid is alkaline, but after only one hour when the reaction is acid; the nature of the changes involved appears to be different in the two cases. Tables and curves are given showing the influence of hydrion concentrations between $p_H = 9·5$ and 4·5 on the denaturation of albumin and ψ-globulin when their aqueous solutions are heated for six hours at 57·5°. Further tables show the precipitating power of various concentrations of ammonium sulphate with respect to solutions of albumin and ψ-globulin, of reaction $p_H = 8$, before and after heating for six hours at 57·5°. From the observations made, it is concluded that in the concentration of antitoxic sera by methods involving thermal denaturation of the proteins, the preliminary heating at 57·5° should be continued for four to five hours if the reaction of the serum is on the alkaline side of $p_H = 7$. By employing ammonium sulphate at 44% instead of 50% of saturation for the precipitation of the second fraction from thermally denaturated sera, complete precipitation of the ψ-globulin (and therefore of the antitoxin) is attained, whilst the proportion of albumin appearing in the second fraction is considerably reduced. The final product is thereby rendered lighter in colour and more potent.   J. H. L.

The Formation of Lactose from Starch by the "Loosened" Ferments of Sucrose Serum. F. RÖHMANN (*Biochem. Zeitsch.* 1917, **84**, 399—401).—The parenteral injection of sucrose into rabbits gives rise to special ferments in the serum ("hervorgelockte Fermente"). The extract of the liver of a rabbit thus treated acts on soluble starch, causing degradation and producing, amongst other products, lactose.   S. B. S.

Occurrence of Lichenase in the Digestive Tract of Invertebrates. MINNA E. JEWELL and HOWARD B. LEWIS (*J. Biol. Chem.*, 1918, **33**, 161—167).—Lichenin, the complex carbohydrate in Iceland moss, is readily hydrolysed by the enzyme lichenase, which is found in various invertebrates, but not in vertebrates. The enzyme occurs usually in the pancreas, but in smaller animals

the alimentary tract may be taken as a whole for the preparation of the enzymic extract. The behaviour of the pancreatic extract to lichenin constitutes therefore a chemical method of differentiating between vertebrate and invertebrate animals. H. W. B.

The Inter relation of the Surviving Heart and Pancreas of the Dog in Sugar Metabolism. A. H. CLARK (*J. Exp. Med.*, 1917, **26**, 721—724; from *Physiol. Abstr.*, 1918, **2**, 678—679).— When the pancreas of a dog is perfused aseptically with Locke's solution containing physiological concentration of dextrose, the optical rotation of the perfusate is diminished, but its reducing power is unaltered. Similar results are obtained when a mixture of dextrose and sugar-free pancreatic perfusate is incubated, and the osazones from these perfusates have lower m. p.'s than glucosazone. When a pancreatic perfusate containing dextrose is circulated through the living heart, the above changes occur, and in addition the reducing properties of the perfusate are altered. These phenomena are believed to be due to an enzyme or enzymes obtained from the perfused pancreas. It is suggested that these enzymes have a specific action on dextrose, lævulose being unchanged when perfused, and that they are responsible for the preparation of that sugar for normal utilisation. Nothing definite can be stated as to the degree of condensation produced or the nature of the polysaccharides formed. W. G.

Influence of Thyroid-feeding on Carbohydrate Metabolism. I. Storage and Mobilisation of the Liver Glycogen in Thyroid-fed Animals. II. Amount of Adrenaline in the Adrenals of Thyroid-fed Rats. III. Acidosis in Experimental Hyperthyroidism and its Relation to Adrenaline in the Blood and the Decrease of Liver Glycogen. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **33**, 193—205, 207—213, 215—227).—Feeding an animal with thyroid gland causes a rapid disappearance of glycogen from the liver. The author now shows that a formation of glycogen in the liver of an animal fed on thyroid gland and carbohydrate occurs only when the amount of carbohydrate administered is exceedingly large. The increased diastatic activity of the liver which these results indicate may be due to the acidosis which is likewise induced by feeding with thyroid gland, although the simultaneous administration of sodium hydrogen carbonate fails to depress the diastatic activity as it does in the normal animal. There does not seem to be any connexion between hyperthyroidism and excessive activity of the adrenals. The amount of adrenaline in the adrenals of animals fed with thyroid gland is not greater than in those of normal animals; the glands are also not increased in size. H. W. B.

Nutritive Factors in Animal Tissues. I. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1917, **32**, 309—323).— Preparations of muscle (meat extract, meat powder, etc.) contain

protein suitable for nutritional purposes, but are unable to pro-
mote the growth of rats, owing to a lack of the water-soluble
vitamine. Dried pig's liver contains both protein and vitamine,
and charts are given which depict the rapid growth which occurs
when this material is the sole source of protein in the diet.

<div align="right">H. W. B.</div>

**Composition and Digestive Activity of Different Fractions
of the Pancreas. II.** R. A. NELSON and J. H. LONG (*J. Amer.
Chem. Soc.*, 1917, **39**, 1766—1778. Compare A., 1915, i, 1025)
—A more complete account of the distribution of the enzymes in
the three layers into which minced pancreas can be separated by
centrifugation at a very high speed. Amylopsin is mostly found in
the middle, liquid layer, which is more active than the non-centri-
fuged pancreas; trypsin is found in all the fractions, but chiefly
in the solid ones; lipase and esterase are mainly present in the
solid layers. The pancreas of the hog, compared with that of the
ox or sheep, is chiefly remarkable for the enormous amylolytic
activity of its liquid layer, whilst it also exceeds these in lipolytic
power. The proportions of fatty, liquid, and protein layers in the
three cases are also recorded, and analyses given of the soluble solids
found in the liquid layer.

<div align="right">J. C. W.</div>

The Physical Chemistry of Cell Membranes. L. BERCZELLER
(*Biochem. Zeitsch.*, 1917, **84**, 59—74).—The tendency of sub-
stances to accumulate at the surface of cells is discussed in con-
nexion with the surface tension of solutions. Stalagmometric
measurements of extracts of organs are given.

<div align="right">S. B. S.</div>

The Action of Animal Tissue on Methylene-blue. T.
THUNBERG (*Skand. Arch. Physiol.*, 1917, **35**, 163—195; from
Physiol. Abstr., 1918, **2**, 655).—A detailed study of the dehydro-
genation of succinic acid by "dehydrogenase" and methylene-blue,
and a full theoretical discussion of the reaction (compare this vol.,
ii, 87).

<div align="right">W. G.</div>

Theory of the Biochemical Action of Light. C. NEUBERG
and K. SCHWARZ (*Berlin. Klin. Woch.*, 1917, **54**, 84—87; from
Physiol. Abstr., 1918, **2**, 584).—The non-photosensitive substances
of animal and plant tissue become photosensitive in the presence
of certain inorganic salts, particularly those of iron. These salts
act as photocatalysts, taking oxygen from the air and passing it
on to the organic light receptors. Under these conditions, leuco-
compounds and quinol pass into the quinonoid form, the change
being reversible. Proteins are also affected. This photosensitivity
is increased by the application of mineral waters containing heavy
metals.

<div align="right">W. G.</div>

The Possible Origin of the Toxicity of Ultra-violet Light.
F. I. HARRIS and H. S. HOYT (*Science*, 1917, **46**, 318—320; from
Physiol. Abstr., 1918, **2**, 656).—Paramœcia were experimented

with. Ultra-violet rays are detoxicated by passage through solutions of gelatin peptone, aminobenzoic acid, cystine, tyrosine, and leucine, the protective action of tyrosine being exceptionally marked in alkaline solution. Solutions of other substances investigated had no appreciable effect. These results agree with the view that the susceptibility of protoplasm to ultra-violet light is conditioned by the selective absorption of the toxic rays by the aromatic amino-acid radicles of the protoplasm.   W. G.

Proteins of Cow's Milk. THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*, 1918, **33**, 7—17).—After the caseinogen has been removed from skim milk by precipitation with dilute sulphuric acid, the remaining proteins are thrown out by saturation with ammonium sulphate, and subsequently separated by treatment with magnesium sulphate. Lactoglobulin is insoluble in saturated magnesium sulphate solution, and contains 2·2% of phosphorus. When it is digested with alcohol, a phosphatide appears to be split off, and the remaining coagulated lactoglobulin now contains only 0·24% of phosphorus. A similar cleavage of phosphatide from vitellin occurs when it is treated with alcohol, and the authors suggest that these so-called globulins are really lecithalbumins or mixtures of proteins. Lactalbumin is soluble in saturated magnesium sulphate solution, and is practically free from phosphorus.

Although traces of proteoses can always be isolated from cow's milk, it is uncertain whether these substances are present as such in the fresh milk or are formed from the proteins by the reagents employed for their isolation. The " nucleon " described by Siegfried (A., 1897, ii, 219) is shown by the authors to consist probably of a mixture of uncoagulable protein and a still unidentified organic substance which yields phosphoric acid on hydrolysis.

By extraction of precipitated caseinogen with alcohol, a new *protein* is obtained which resembles the gliadin of wheat in its solubility in 50 to 80% alcohol. [See also *J. Soc. Chem. Ind.*, 1918, March.]   H. W. B.

The Excretion of Substances Foreign to the Organism in the Urine. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 75—79).—Attention is directed to the fact that in the case of foreign substances excreted as conjugated or otherwise altered derivatives, the surface tensions of the latter in aqueous solution are greater than that of those of the former. Examples : benzoic acid and hippuric acid, menthol and menthol glycuronate, phenol and phenolsulphonic acid, phenol, catechol, and quinol.
     S. B. S.

Citric Acid in Urine. S. AMBERG and W. B. McCLURE (*Amer. J. Physiol.*, 1917, **44**, 453—462; from *Physiol. Abstr.*, 1918, **2**, 683).—Citric acid can be detected in human urine by Kunz's pentabromoacetone method, or by Salant and Wise's method, a modification of Denigès's reaction. Preliminary experiments

indicate that about 500 mg. of citric acid are voided daily in the urine.   W. G.

Salicylates. IX. Question of Salicyluric Acid in Salicyl Urines. PAUL J. HANZLIK (*J. Pharm. Exper. Ther.*, 1917, **10**, 461—490).—The author has been unable to isolate any salicyluric acid from urines after administration of salicylic acid, although all the methods for its isolation which have been published have been employed. In each case, only impure salicylic acid containing no glycine has been obtained. It appears improbable, therefore, that salicylates are converted into salicyluric acid in the human or animal organism.   H. W. B.

Acidosis. IX. Relationship between Alkali Retention and Alkali Reserve in Normal and Pathological Individuals. WALTER W. PALMER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **32**, 499—507. Compare A., 1917, i, 523).—In normal persons, the urine becomes more alkaline than the blood ($p_H = 7\cdot4$) when the carbon dioxide present as hydrogen carbonate in the plasma exceeds 71 ± 5 volumes per cent. In most pathological cases, the urine does not become more alkaline than the blood until a higher level of hydrogen carbonate has been reached than in normal individuals. If, therefore, the administration of sodium hydrogen carbonate to a patient is continued until the urine turns alkaline, unnecessarily large and perhaps injurious quantities of hydrogen carbonate may be given. The therapeutic use of sodium hydrogen carbonate should therefore be controlled by estimations of the hydrogen carbonate in the plasma.

The alkali retention test (feeding with sodium hydrogen carbonate until the urine shows an alkalinity of $p_H = 7\cdot4$) indicates a greater acidosis than actually exists. If a positive result is obtained, it should be confirmed by blood analysis before being accepted.   H. W. B.

The Nitrogenous Extractives of Tumours. JACK CECIL DRUMMOND (*Biochem. J.*, 1917, **11**, 246—254).—Four kinds of tumours of human and avian origin were extracted with boiling water, and after treatment with basic lead acetate the extracts were investigated in respect of their nitrogenous constituents. In general, the purine fraction was largest; adenine was found in all cases, and guanine, xanthine, and hypoxanthine in some. Small quantities of histidine, carnosine, and (probably) arginine were isolated from the avian tumour (Rous chicken sarcoma). Tyrosine and creatinine were present in all, and leucine in most cases (compare A., 1916, i, 866).   J. H. L.

Formation of Creatine. Effects on the Excretion of Creatine in the Bird produced by Paraformaldehyde and Hexamethylenetetramine given separately and combined with Arginine Carbonate and other Substances. WILLIAM HENRY THOMPSON (*Biochem. J.*, 1917, **11**, 307—318).—It is suggested that formaldehyde, which probably takes part in the pro-

duction of methylated compounds, such as betaine, in plants and in the muscles of invertebrates, is formed also in the muscle tissue of vertebrates, and is disposed of by combination with a guanidine nucleus to form creatine.   The increased excretion of creatine following the administration of arginine to ducks with their food (A., 1917, i, 673) becomes greater if paraformaldehyde is administered at the same time, although the latter alone has no effect.   Paraformaldehyde ingested together with glycine, sarcosine, or guanidine carbonate also increases the production of creatine. Very much larger increases (in some cases six to eight times the normal amount) are produced by subcutaneous injection of para-formaldehyde alone or with arginine.   Hexamethylenetetramine produces similar effects.   The mechanism of the formation of creatine from arginine and formaldehyde in vivo is represented as involving conversion of the arginine into glycocyamine (compare Baumann and Hines, A., 1917, i, 677), methylation of the amino-group of the latter by interaction with two molecules of form-aldehyde (compare Werner, T., 1917, **111**, 844), and isomeric change of the product into creatine by migration of the methyl group.   J. H. L.

Lacquer Poisoning. I. TOYAMA and T. KAYABA (*Hifukwa Hitsunyokikwa Zasshi*, 1916, **16**, No. 7, 7—10; from *Physiol. Abstr.*, 1918, **2**, 693).—Lacquer poisoning may be produced in susceptible individuals by passing near a lacquer tree or through a store containing lacquered articles.   The poisoning is probably not due to a volatile constituent.   The chief constituent of lacquer is urushiol, the chief poison having the composition $C_{15}H_{27} \cdot C_6H_3(OH)_2$. Lacquer also contains a hydrated and a methylated urushiol which are toxic, and a dimethylated and a hydro-dimethylated urushiol which are non-toxic (compare Majima, A., 1908, i, 437; 1909, i, 402, 945; 1912, i, 883).   W. G.

Surface Tension of Solutions of Alkaloids. L. BERCZELLER and M. SEINER (*Biochem. Zeitsch.*, 1917, **84**, 80—105).—Stalagmo-metric measurements of solutions of salts of alkaloids, with addi-tions of varying amounts of alkali, carried out with the object of illustrating Traube's theory of the connexion between surface tensions of solutions and toxic action.   S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Enzymes concerned in the Decomposition of Dextrose and Mannitol by Bacillus coli communis. II. Experiments of Short Duration with an Emulsion of the Organisms.
EGERTON CHARLES GREY (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 75—92. Compare A., 1914, i, 1034).—An emulsion of *B. coli communis*

in saline solution containing an amount of bacteria which would weigh, when dry, 1 gram, is sufficient completely to ferment 40 grams of dextrose in forty-eight hours in the presence of calcium carbonate. The author describes an ingenious device to prevent the settling of the latter during the experiment. The calcium carbonate is sewn up in small sacks of cloth, in each of which is placed also a small cork, the weights being so adjusted that the sacks just sink to the bottom of the flask when they are first introduced. During the course of the fermentation, the acid disengaged penetrates the sacks, and they become swollen with gas and rise to the top of the solution. During this movement up and down, the calcium carbonate contained in the sacks becomes gradually liberated, so that the solution is always turbid with calcium carbonate without being mechanically agitated from without. At the end of the experiment, the products of fermentation, namely, alcohol, carbon dioxide, formic, acetic, lactic, and succinic acids, are estimated in the solution. The actual amount of any of the products obtained is dependent on the concentration of salt and the temperature of fermentation. By comparison of the various amounts produced in different experiments, it is found that succinic acid and acetic acid are complementary as regards the extent of their formation, and are therefore probably produced from a common parent substance. Acetic acid and alcohol and alcohol and succinic acid are similarly related to one another, so that it would appear that the three substances, alcohol, acetic acid, and succinic acid, are formed from a common intermediate substance by the action of the same enzyme. The formation of lactic acid appears to be quite independent of that of the other products of fermentation, and its production is therefore due to a separate enzyme. The addition of peptone to the culture medium containing dextrose leads to the production of a greater proportion of lactic acid and a lesser proportion of alcohol, acetic acid, and succinic acid.

The products of the bacterial decomposition of mannitol closely resemble in amount those obtained from dextrose, which is in harmony with the author's view that the fermentation of various carbohydrates and allied substances by bacteria is effected by a single set of enzymes the action of which is common to all such cases of fermentation. The first step in the degradation of a particular molecular structure may require a special enzyme to produce the common intermediate substance, but the subsequent changes are always similar, being due to the action of the standard series of bacterial enzymes. [See also *J. Soc. Chem. Ind.*, 1918, 103A.]   H. W. B.

Enzymes concerned in the Decomposition of Dextrose and Mannitol by Bacillus coli communis. III. Various Phases in the Decomposition of Dextrose by an Emulsion of the Organisms. EGERTON CHARLES GREY *(Proc. Roy. Soc,* 1918, [*B*], **90**, 92—106. Compare preceding abstract).—By examining portions of a fermenting solution containing dextrose and bac-

teria at the end of twelve, twenty-four, forty-eight, and seventy-two hours respectively, it is found that during the first twelve-hour period the number of living bacteria diminishes very rapidly, whilst during the second period a still more rapid growth of bacteria sets in, so that at its close the number present greatly exceeds that at the commencement of the experiment. Corresponding with these changes, there is a cessation in the production of lactic acid in the first period, the chief products being carbon dioxide, alcohol, and acetic and succinic acids, whilst subsequently in the third period, when the number of bacteria is at a maximum, the production of lactic acid is so much accelerated that it forms 70% of the fermented sugar. The period of exalted bacterial growth is associated with the transformation of a large proportion of the dextrose into a complex carbohydrate, which only reduces Fehling's solution after hydrolysis. The extent of the synthesis during this period is quantitatively of the same order as the degradation which ensues in the following period. A synthesis of fat was also observed on one occasion in circumstances which could not be again realised.

Since the amount of sugar decomposed during the first period in which the rapid diminution in the number of living cells occurs is as great as during the third period, in which the number of living cells both at the start and at the finish is enormously greater, the author draws the conclusion that the fermentation is brought about, not by the cells as such, but by enzymes in the cells. This conclusion is confirmed by the fact that different conditions result in variations in the amounts of the products of fermentation due presumably to the varied influence of the altered conditions on the operation of the different enzymes present. [See also *J. Soc. Chem. Ind.*, 1918, 103a.]   H. W. B.

Influence of Conditions of Bacterial Cleavage of Proteins on the Cleavage Products. TAKAOKI SASAKI (*J. Biol. Chem.*, 1917, **32**, 527—532).—When *l*-tyrosine is acted on by *Bacillus coli communis* or *B. proteus vulgaris*, the chief product obtained depends on the composition of the medium employed. In the presence of lactose *p*-hydroxyphenylethylamine is produced, whilst if the lactose is replaced by Henderson's phosphate mixture, the same bacteria form *d*-*p*-hydroxyphenyllactic acid without any trace of the amine.   H. W. B.

Stereochemistry of the Bacterial Decomposition of Albumin. TAKAOKI SASAKI and ICHIRO OTSUKA (*J. Biol. Chem.*, 1917, **32**, 533—538).—When *B. proteus vulgaris* or *B. coli communis* acts on *d*-tyrosine, *d*-*p*-hydroxyphenyllactic acid is formed. If now *B. subtilis* is substituted for either of the above bacilli, the product is *l*-*p*-hydroxyphenyllactic acid. The author suggests that an intermediate substance, probably of a ketonic nature, is first formed, which is then completely converted into one or other of the two possible asymmetric products.   H. W. B.

Biochemical Study of Proteus vulgaris, Hauser. Comparison of the Properties of a Pathogenic Race and of a Saprophytic Race. F. G. VALLE MIRANDA (*Compt. rend.*, 1918, **166**, 184—187).—A comparison by ponderal methods of the biochemical properties of a *Proteus* isolated in a case of acute infantile gastro-enteritis. and of another found in putrefying meat. These have been compared with respect to their behaviour towards carbohydrates, glycerol, gelatin, amino-acids, and tryptophan, and the results indicate that, despite their different origin, the two *Proteus* examined constitute two races of *Proteus vulgaris*, and not two distinct species.   W. G.

Biochemistry of Pathogenic Anærobes. II. The Acid Production of Bacillus Welchii (B. perfringens) and Bacillus sporogenes (Metchnikoff). CHARLES GEORGE LEWIS WOLF and STEPHEN VEITCH TELFER (*Biochem. J.*, 1917, **11**, 197—212).—Dyer's method (A., 1917, ii, 157) was applied to the investigation of the volatile acids formed by *B. perfringens* and *B. sporogenes*, under anærobic conditions, in milk and in peptone broth containing 2% of dextrose. It was found that for the identification of the constituents of an unknown mixture of volatile acids the method must be applied, not only to the original mixture, but also to certain distillation fractions or even to secondary fractions. By this means useful comparative data may be obtained in the investigation of a number of mixtures, especially if the curves plotted are compared with those corresponding with mixtures of known composition; but very tedious fractionation would be required to obtain quantitative results, or even to detect such an acid as propionic in presence of acetic and butyric acids. The colour tests recommended by Dyer cannot be depended on until the acids have been separated.

The results of the present investigation indicate that in milk *B. sporogenes* forms acetic, butyric, valeric, and hexoic acids, probably in the approximate proportions 25:17:16:41, whilst *B. perfringens* forms only acetic and butyric acids in the proportions 2:3. In the dextrose–peptone broth both organisms produce only acetic and butyric acids, in the proportions 3:2. These figures are given with great reserve; considerable amounts of propionic acid may have been present in all cases without being detected. For both organisms in milk the volatile acids constituted 68—69% of the total acids produced (both expressed in terms of alkali); for *B. sporogenes* and *B. perfringens* in dextrose–peptone the corresponding values were 55% and 50% respectively.   J. H. L.

Biochemistry of Pathogenic Anærobes. III. The Effect of Acids on the Growth of Bacillus Welchii (B. perfringens) and Bacillus sporogenes (Metchnikoff). CHARLES G. L. WOLF and JOHN EDMUND GUY HARRIS (*Biochem. J.*, 1917, **11**, 213—245). —After an investigation of the effect of addition of different quantities of various acids on the reaction of peptone broth containing 2% of dextrose, the authors studied the influence of the initial reaction

of the medium, adjusted to various values between $p_H = 6\cdot5$ and $4\cdot5$ by addition of acid, on the anærobic fermentation of *B. perfringens* and *B. sporogenes*. The acids employed were hydrochloric, formic, acetic, butyric, lactic, malic, and succinic.   The main conclusions drawn may be summarised as follows.

The higher the initial hydrion concentration in the medium, the longer is the latent period of growth, *i.e.*, the time elapsing between inoculation and the first visible signs of growth; and if the initial hydrion concentration exceeds a certain critical value (about $p_H = 4\cdot8$ for *B. perfringens* and $p_H = 4\cdot9$ for *B. sporogenes*) no fermentation occurs. Where fermentation takes place, the final reaction attained is not a "physiological constant," but varies within comparatively narrow limits ($p_H = 4\cdot2$—$4\cdot8$ for *B. perfringens* and $p_H = 4\cdot9$—$5\cdot5$ for *B. sporogenes*), according to the initial reaction of the medium.   Moreover, the form of the curve representing the dependence of final on initial reactions, designated the "reaction resultant," is to a certain extent characteristic of the particular acid to which the initial reaction is due.   The change in the value of p_H during fermentation is not a measure of the amount of acids produced.   In the case of *B. perfringens*, the production of acids and carbon dioxide is practically independent of the initial reaction when the latter is due to hydrochloric acid. With feebly dissociated acids, on the other hand, much larger amounts are required to produce the same initial hydrion concentrations, and these acids appear to exert an inhibitive influence on fermentation apart from that due to their cations.   *B. sporogenes* differs from *B. perfringens* in that, in media of which the initial reaction is near the critical point, the final reaction may be less acid than the initial.   This is attributed to the production of large amounts of basic and amphoteric substances which reduce the acidity and act as buffers.   Cessation of growth is probably due almost entirely to accumulation of metabolites.

It is suggested that by treatment of gas gangrene infections by means of highly buffered solutions with hydrion concentrations slightly above the critical value, growth might be inhibited.

<div align="right">J. H. L.</div>

Ptomaines and War Wounds.   Albert Berthelot (*Compt. rend.*, 1918, **166**, 187—189).—The author has endeavoured to show that toxic ptomaines may be formed by the action, on the blood, of proteolytic and amino-acid splitting microbes likely to be found in wounds, and considers that his experimental results support this idea.   W. G.

The Autolysis of Yeast and the Influence of its Products of Proteolysis on the Development of Yeast and of Lactic Bacteria.   Paul Vansteenberge (*Ann. Inst. Pasteur*, 1917, **31**, 601—630).—After death the yeast-cell loses its cell water and diminishes in size.   If the enzymes present have not been destroyed after a time varying with the temperature, liquefaction of the yeast occurs.   For the endotryptase the optimum temperature is

45—50° and the maximum temperature 53°. For autolysis of yeast in the living state the optimum temperature is 48—50°. The progress and completion of the autolysis are best shown by an increase in the acidity to a certain maximum and the separation of tyrosine in a crystalline state from the autolysate. When yeast is boiled with water, the extract only contains one-third of the total nitrogen, but if the boiling is preceded by an autolysis at 48° lasting twenty-three hours, the whole of the nitrogen is obtained in a form soluble in water and not coagulated by heat. An extract of autolysed yeast is much more nutritive for yeast and for lactic bacteria than an extract of fresh yeast, and the nitrogen is converted by the autolysis into a form more readily assimilable by these organisms.

In an extract of autolysed yeast of a strength equivalent to 20 grams of yeast per 100 c.c., there are certain products unfavourable to the development of yeast, but this injurious action disappears on dilution. Such products are tyrosine and leucine, of which the former is injurious at concentrations over 0·05% and the latter at concentrations above 0·08%. At the concentrations at which these substances are present in autolysed yeast they inhibit the development of yeast, but do not exert any unfavourable influence on lactic bacteria. [See also *J. Soc. Chem. Ind.*, 1918, 103A.]

W. G.

The Action of Arsenic Salts on Yeast. F. Boas (*Zeitsch. Gärungsphysiol.*, 1917, **6**, 1—12; from *Physiol. Abstr.*, 1918, **2**, 631).—Sodium metarsenite retards fermentation by living yeast. Fermentation is at first arrested by alkali arsenates, but, in the presence of soluble nitrogen, it is promoted after five to seven hours. Although in nitrogen-free solutions the inhibiting action is very strong, yet in some cases after twenty-four hours fermentation had proceeded under these conditions. Owing to different physiological conditions of the yeast, considerable variation in the results was noticeable.   W. G.

The Water-soluble Accessory Growth-promoting Substance in Yeast. JACK CECIL DRUMMOND (*Biochem. J.*, 1917, **11**, 255—271).—The opinion of McCollum and Kennedy (A., 1916, i, 451), that the "water-soluble growth-promoting factor B" is identical with the antineuritic vitamine, is confirmed, inasmuch as it is now shown, by feeding experiments with rats, that the water-soluble factor in yeast possesses many of the properties of the antineuritic principle, such as insolubility in ether or absolute alcohol, and relative insensitiveness towards heat, dilute acids, and alkalis. Unsuccessful attempts to isolate the active substance from yeast are described. The water-soluble factor is not identical with adenine, nucleic acid, or any of the constituents of commercial meat extract. [See also *J. Soc. Chem. Ind.*, 1918, 134A.]

J. H. L.

Intermediary Reactions in Alcoholic Fermentation. H.
EULER, HJ. OHLSEN, and D. JOHANSSON (*Biochem. Zeitsch.*, 1917,
84, 402—406).—A Swedish beer-yeast was dried at 40°, and ex-
tracted with water. Such an extract contains a phosphatase, which
acts directly on lævulose. Dextrose is not, however, acted on by it
unless previously treated with fresh yeast. A Swedish yeast,
weakened by being kept for six weeks in a solution containing
sodium chloride, sugar, but no nitrogen, could esterify lævulose
but not dextrose. The results confirm Harden's view (compare
A., 1908, i, 590) that the hexose phosphate is a derivative either
of lævulose or of a closely allied sugar, and that the dextrose must
be converted into this in order to form the phosphate ester.

S. B. S.

**Is Lactic Acid an Intermediate Product of Alcoholic
Fermentation ?** ALEXANDRE LEBEDEV (*Biochem. J.*, 1917, **11**,
189—196).—The balance of experimental evidence is considered to
be unfavourable to the view that lactic acid is an intermediate
product of fermentation. The conclusions of Palladin and Sabinin
on this subject (A., 1916, i, 620) are criticised. In the decomposi-
tion of lactic acid by yeast-reductase in presence of methylene-blue
the quantity of acetaldehyde formed is much smaller than corre-
sponds with the equation given (*loc. cit.*), and when pyruvic acid
is substituted for methylene-blue very little alcohol is formed in
comparison with the amount of carbon dioxide. Pyruvaldehyde is
a more probable intermediate product of fermentation than lactic
acid, for at very low concentrations it is decomposed by yeast into
practically equivalent amounts of alcohol and carbon dioxide, but,
on the other hand, it is fermented only very slowly and is toxic
towards yeast enzymes. The evidence regarding the possible
formation of pyruvic acid in the course of alcoholic fermentation
is inconclusive.   J. H. L.

**Influence of Metallic Salts on Germination in the Presence
of Calcium.** L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1918,
166, 89—92).—A continuation of previous work (compare A.,
1917, i, 530), the peas being germinated in water containing the
various salts examined, either with or without the addition of
calcium in the form of its sulphate or chloride. The root measure-
ments show that the presence of any salt, in amount approaching
the toxic quantity in pure water, lessens or prevents the favour-
able action exerted by calcium when present alone. Thus the
different metals, whether toxic or alimentary, function as antagon-
ists to calcium in germination, in the same way as calcium behaves
as an anti-toxic towards them. The physiological action of a mix-
ture is thus not equal to the sum of the actions of its constituents.

W. G.

Action of Acids on Plants. I. ONODERA (*Ber. Ohara Inst.
Landw. Forsch.*, 1916, **1**, 53—100; from *Physiol. Abstr.*, 1918, **2**,

707).—In general, plant growth was considerably stimulated by moderately concentrated acids, and in particular by nitric acid in the form of carbamide nitrate containing 0·05 gram per litre. The acids investigated, arranged in descending order of toxicity, were: hydrochloric, sulphuric, formic, butyric, acetic, nitric, and α-hydroxypropionic. Plants grown in an acid culture develop abnormally in height, their root development being quickly arrested, but the growth of the foliage is continuous.　　W. G.

The Effect of certain Organic Compounds on Plant Growth. M. J. FUNCHESS (*Alabama Agric. Expt. Stat. Bull.*, 1916, **191**, 103—132; from *Physiol. Abstr.*, 1918, **2**, 707—708).—Pot experiments were conducted to determine the effect of coumarin, vanillin, pyridine, quinoline, dihydroxystearic acid, and pyrogallol on plant growth in the case of oats and wheat grown on red clay or a sandy soil. Pyridine and quinoline were found to be beneficial in the soils used. The compounds used in small amounts were not found to be harmful to growth. Vanillin applied at the rate of 5—10 parts per 10,000 was quite harmful to oats grown on the sandy soil, in the, presence or absence of complete fertilisers, but there was no residual harmful effect. Similar results were obtained with coumarin. The conclusion is drawn that rapid chemical or biochemical transformation of these compounds into inert forms occurs in unsterilised soils under the above experimental conditions, and that the results obtained with soil cultures do not agree with those obtained with solution cultures.　　W. G.

Action of Various Fertilisers, especially Manganese Sulphate, on the Growth of Oats. L. HILTNER and G. KORFF (*Prakt. Blätt. Pflanzenbau & Pflanzenschutz*, 1917, **15**, 549—556; from *Bied. Zentr.*, 1918, **47**, 15—19).—The authors describe pot experiments in which oats were grown in various types of soils, some of which were treated with iron, copper, or manganese sulphates, or with sulphur, and all received guano. The addition of manganese sulphate caused in each case an increase in the size of the plant and in the total number of oat-grains, especially in soils containing much humus. In peaty soils, the yield of oat-grains was seventy times as great in the presence of manganese sulphate as in its absence. It is suggested that these remarkable results are largely due to the accelerating action of manganese on the oxidation of the guano added to the soil. The other sulphates and the sulphur experimented with produced similar, but not such marked results. [See also *J. Soc. Chem. Ind.*, 1918, March.]

H. W. B.

The Necessity for an Acceptor of Hydrogen and an Acceptor of Oxygen for the Manifestation of the Processes of Oxido-reduction in Organic Liquids of Animal and Vegetable Origin. J. E. ABELOUS and J. ALOY (*Compt. rend.*, 1918, **166**, 130—132).—It has been shown by Bach (compare A., 1917, i, 375, 431) that the presence of a readily oxidisable sub-

stance is necessary for the reduction of alkali nitrates by milk or potato juice, and the authors now show that the presence of a readily reducible substance is essential for oxidation under similar conditions. W. G.

The Relationship between the Osmotic Concentration of Leaf Sap and Height of Leaf Insertion in Trees. J. ARTHUR HARRIS, ROSS AIKEN GORTNER, and JOHN V. LAWRENCE (*Bull. Torrey Bot. Club*, 1917, **44**, 267—286 [reprint]).—Measurements have been made on leaves gathered from different heights on twenty-six trees belonging to twelve species. The results indicate that the osmotic concentration of the leaf sap, as determined by the freezing-point lowering method, increases from lower to higher levels. The specific electrical conductivity, K, shows a tendency to decrease from lower to higher levels, but the results obtained are not very regular. The ratio K/Δ, where Δ is the lowering of the freezing point, however, shows a regular decrease from lower to higher levels. The authors have endeavoured to establish a formula showing the relationship between the increase in osmotic concentration and the difference in heights of insertion of the leaves plus the resistance to the passage of water moving at the rate of the transpiration stream opposed by conducting tracts equal in length to the differences in the heights of insertion. The value for the latter factor is, however, not yet definitely established.

W. G.

Genesis of Inulin in Plants. H. COLIN (*Compt. rend.*, 1918, **166**, 224—227).—Estimations of the total sugar, reducing sugar, sucrose, starch, and inulin in the various organs of the plant in the case of chicory, dahlias, and Jerusalem artichokes show that there can be no question of the immediate elaboration of inulin by the leaf and of its migration, as such, to the subterranean organs. The leaves only deliver to the plant the sugars the condensation of which takes place in the stem or only in the tubercles or the roots.

W. G.

The Constituents of Wood which give Colour Reactions. II. H. WICHELHAUS and MARTIN LANGE (*Ber.*, 1917, **50**, 1683—1685. Compare A., 1916, i, 874).—About 98 litres of distillate have been collected from 1200 grams of pine or fir wood by the passage of a current of steam at 180—200°, and separated by a second distillation into two fractions. The first two-thirds gave a green precipitate with phloroglucinol and hydrochloric acid, whilst the last third gave the typical cherry-red precipitate, and also formed a brick-red *substance*, $C_{18}H_{18}O_7N_6$, with *p*-nitrophenylhydrazine. The latter is apparently a condensation product of a ketofurfuraldehyde, $C_6H_8O_5$, derived from a hexose as follows: $C_6H_{12}O_6 - H_2O + O = C_6H_8O_5 + H_2O$. [See also *J. Soc. Chem. Ind.*, 1918, March.]

J. C. W.

The Constituents of the Bark of the Hymenodyctyon excelsum. CHARLES STANLEY GIBSON and JOHN LIONEL SIMONSEN

(*J. Proc. Asiatic Soc., Bengal*, 1916, [N.S.], **12**, 161 [reprint]).—
The authors have confirmed Broughton's work (1870) in that they
were able to isolate æsculin and scopoletin from the bark of the
Hymenodyctyon excelsum, but they were unable to find any traces
of an alkaloid (compare Naylor, A., 1883, 1141; 1885, 565).

<div align="right">W. G.</div>

The Loganberry and the Acid Content of its Juice.
MILO REASON DAUGHTERS (*J. Ind. Eng. Chem.*, 1918, **10**, 30).—
Analyses are given of the loganberry and of its juice. The chief
acid in the fruit is citric; tartaric and volatile acids are pre-
sent in traces; malic acid is absent. [See also *J. Soc. Chem. Ind.*,
1918, March.]

<div align="right">L. A. C.</div>

Soil Acidity and the Hydrolytic Ratio in Soils.
C. H. SPURWAY (*J. Agric. Research*, 1917, **11**, 659—672).—The examina-
tion of a number of soils from glacial formations indicates that the
reaction of these soils is probably determined chiefly by the hydro-
lytic ratio between salts of the alkaline earth metals on the one
hand and those of iron and aluminium on the other, when these
are in equilibrium; the hydrolytic ratio depending on the concen-
tration and degree of hydrolysis of each salt in the presence of the
other when equilibrium is reached. [See also *J. Soc. Chem. Ind.*,
1918, 132A.]

<div align="right">W. G.</div>

Isolation of *p*-Hydroxybenzoic Acid from Soil.
E. H. WALTERS (*J. Amer. Chem. Soc.*, 1917, **39**, 1778—1784).—
p-Hydroxybenzoic acid and benzoic acid have been isolated from a
soil in the orange groves of Florida. The soil is largely composed
of quartz sand mixed with organic matter, which can be almost
entirely removed by washing with dilute sodium hydroxide. The
actual quantities of the pure acids obtained correspond with about
21·6 parts of *p*-hydroxybenzoic acid and 1·7 parts of benzoic acid
per million.

<div align="right">J. C. W.</div>

Alkali Soils : Biochemical Factors in their Reclamation.
J. H. BARNES and B. ALI (*Agric. J. India*, 1917, **12**, 368—380;
from *Physiol. Abstr.*, 1918, **2**, 712).—Ordinary alkali land con-
tains all the organic life associated with soil fertility, but in a more
or less dormant state. In the more saline soils of long duration
the vitality of these organisms is somewhat impaired. Nitrifying
organisms are thus dormant in alkali soils so long as the saline
matter is in excess, but washing of such soils is followed by increased
nitrification, and this will commence before the soil is sufficiently
washed to admit of the growth of crops, as nitrifying organisms can
exist in a solution of higher osmotic pressure than can the higher
plants. Ammonifying organisms are still more hardy than the
nitrifying organisms to saline matter. There is an indication that
the activity of nitrogen-fixing bacteria of the *Azotobacter* type is
increased after washing.

<div align="right">W. G.</div>

Organic Chemistry.

Solubility of Lead Acetate in Water. YUKICHI OSAKA and REIJIRO HARA (*Mem. Coll. Sci. Kyoto,* 1917, **2**, 147—150).— Measurements have been made of the solubility of lead acetate in 0·025, 0·05, and 0·1N-acetic acid at 25°, 35°, and 45°. The quantity of salt dissolved per 100 grams of water increases slightly with the acidity of the solution, the relation being linear. By extrapolation, the solubility in pure water is found to be 54·38 parts per 100 of water at 25°, 87·77 at 35°, and 154·25 at 45°. These extrapolated values are based on the assumption that the salt is not hydrolysed. H. M. D.

Physical Properties of a Number of Pure Esters. J. HOWARD MATTHEWS and KATHARINE E. FAVILLE (*J. Physical Chem.,* 1918, **22**, 1—21).—The esters, obtained from Kahlbaum, were purified by chemical treatment according to the method described by Young and Thomas (T., 1893, **63**, 1191), and then subjected to fractional distillation in an apparatus devised to give a constant pressure of 760 mm. In accordance with the results obtained by most of the previous observers, the boiling points of the esters were found to extend over an appreciable range. The physical properties measured were the boiling point, density, viscosity, specific inductive capacity, and refractive index, the values being recorded in the table.

	B. p.	D_4^{20}.	$\eta_{20°}$.	$\epsilon_{20°}$.	n_D.
*iso*Amyl formate	... 123·46°—123·56°	0·8773	0·789	4·98	1·39772
*iso*Butyl formate	... 98·15 — 98·25	0·8832	0·638	5·93	1·38568
Propyl acetate	... 101·57 —101·77	0·8869	0·585	8·10	1·38422
Ethyl propionate	... 99·12 — 99·22	0·8904	0·545	5·75	1·38414
Propyl propionate	... 121·0 —121·25	0·8809	0·674	4·66	1·39325
Ethyl butyrate	... 120·0 —120·5	0·8784	0·665	5·91	1·40002
*iso*Butyl valerate	... 167·0 —168·5	0·8544	1·118	8·21	1·40569

The boiling points of the esters at various pressures were also determined, and the results applied in testing the deductions·made by van der Waals in reference to the theory of corresponding states. For ethyl propionate, ethyl butyrate, and *iso*butyl formate, critical data have been previously determined, and by making use of these a comparison is made of the values of the ratios of the absolute temperatures at corresponding pressures to the absolute critical temperatures. For a given pressure, the temperature ratio varies appreciably with the nature of the ester, but the deviations from constancy are less than those found by Young and Thomas in their investigation of a series of ten esters. H. M. D.

Relation between the Affinity Values of the Aliphatic Acids of the Mono- and Di-basic Series. GERVAIS LE BAS (*Chem. News,* 1918, **117**, 121—122).—Tables of the affinity values ($k \times 10^4$)

of monobasic fatty acids, starting with formic acid, and of dibasic fatty acids, starting with succinic acid, are given. The latter form a nearly arithmetical series, that is, the values for $n(k \times 10^4)$, where n represents the position in the series, are very nearly the same. If the numbers for the members of the dicarboxylic acid series be divided by the numbers for the members of the monocarboxylic acid series, a series of numbers is obtained which, when plotted against successive integers, gives a curve resembling a rectangular hyperbola. The free energy due to the carboxylic group in the monobasic acid series diminishes with the increase in the length of the hydrocarbon chain. When two such groups are present in the same molecule the ratio between the affinity values varies inversely with the number of carbon atoms between the groups, except in the case of oxalic and succinic acids, the ratio of which shows a greater increase. In the dicarboxylic acid series the two carboxylic groups are mutually active, the one increasing the tendency of the other to be active or possess residual affinity, but the latter function varies inversely with the number of interposed methylene groups. The following formula for the dicarboxylic acids, in which these facts have been noted, is suggested:

$$\mathrm{CH_2} \!<\! {}^{\mathrm{CH_2 - CH_2 - CO_2H}}_{\mathrm{CH_2 - CH_2 - CO_2H}} \Big)$$
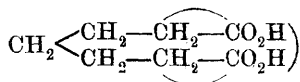
<div align="right">C. A. M.</div>

Method of Preparing Acetaldehyde. UNION CARBIDE Co. (U.S.-P., 1247270, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 74A).—Acetylene is combined with the elements of water in an acid bath containing a mercury compound. The bath is maintained at such a temperature that the acetaldehyde distils continuously, and the mixture of acetaldehyde and acetylene is conducted into a series of baths similar to the first bath.   W. P. S.

The Wagner-Saytzeff Reaction with Mesityl Oxide. C. J. ENKLAAR (*Chem. Weekblad*, 1918, **15**, 188—190).—The liquid obtained by the action of zinc, mesityl oxide, and allyl bromide, in presence of anhydrous ether, yields on distillation two fractions, in addition to unchanged products. The first fraction has b. p. 71°/ 20 mm., and consists of $\beta\delta$-dimethyl-$\Delta^{\beta\epsilon}$-heptadien-δ-ol mixed with a smaller proportion of a ketone, $\mathrm{C_9H_{16}O}$, probably a dimethyl-heptenone.

The second fraction has b. p. 140—142°/3 mm., and its constituents have not been identified.   A. J. W.

Influence of different Compounds on the Destruction of Monosaccharides by Sodium Hydroxide and on the Inversion of Sucrose by Hydrochloric Acid. III. Constitutional Formulæ of the Hydroxybenzoic Acids and of Sulphanilic Acid. H. I. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 581—589. Compare A., 1917, i, 631; this vol., i, 101).— Salicylic acid behaves in alkaline solution as a monobasic acid in

CH
HC⟋⟍C:O
HC⟍⟋CH·CO₂H
CH
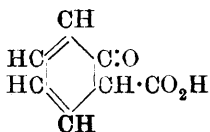
retarding the destruction of dextrose, whereas *m*- and *p*-hydroxybenzoic acids behave as dibasic acids. The author considers that these results support the constitutional formula (annexed) assigned to salicylic acid by Brunner (compare Holleman, " Die direkte Einführung von Substituenten in den Benzolkern," Leipzig, 1910).

Sulphanilic and hippuric acids behave as monobasic acids in alkaline solutions, and are neutral in their influence on the inversion of sucrose by hydrochloric acid. On these grounds the author assigns the constitution I to sulphanilic acid in alkaline solution and constitution II in acid solution.

NH₂   NH₃
  ⬡   ⬡ O
SO₂·OH   SO₂
(I.)   (II.)
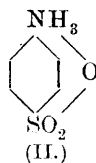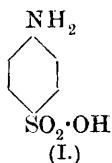
[See also *Ind.*, 189ᴀ.*]   W. G.

Lactose. II. A. SMITS and J. GILLIS (*Proc. K. Akad. Wetensch Amsterdam*, 1918, **20**, 573—580. Compare this vol., i, 101).— From a study of the results previously given (*loc. cit.*), coupled with those obtained by Hudson (compare A., 1909, ii, 131; 1910, i, 220), the authors consider that mutarotation is not due to a slow dehydration process in the sugar series, as was assumed by Hudson, but to the slow establishment of an internal equilibrium between two stereo-isomeric forms. Further, that for the unsubstituted aldoses, such as dextrose, galactose, lactose, etc., the presence of water of hydration does not change anything in the structure of the asymmetric terminal carbon atom. The pseudo-ternary $T - x$ figure of the system water–α-lactose–β-lactose is given, and the surface of equilibrium lying in it is shown.   W. G.

The Reduction of the Group ·CH₂I attached to Nitrogen. AMAND VALEUR and EMILE LUCE (*Compt. rend.*, 1918, **166**, 392—394. Compare this vol., i, 102).—Dimethyliodomethyl-δ-iodo-amylammonium iodide, $CHMeI·CH_2·CH_2·CH_2·NMe_2I·CH_2I$, when reduced by zinc in alcohol or in dilute acetic acid, gave trimethyl-amylammonium iodide, $CH_2Me·CH_2·CH_2·CH_2·NMe_3I$, together with a small amount of an unsaturated methiodide. Methylene-des-dimethylpiperidine iodide when similarly reduced gave des-di-methylpiperidine methiodide [trimethyl - Δ^{δ} - pentenylammonium iodide], m. p. 227—229°, giving an aurichloride, m. p. 107°. Di-methyliodomethyl-Δ^{γ}-pentenylammonium iodide,

$$CHMe:CH·CH_2·CH_2·NMe_2I·CH_2I,$$
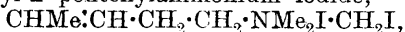
when reduced gave a mixture of two isomeric unsaturated *meth-iodides*, $C_8H_{18}NI$, giving two *aurichlorides*, having m. p.'s 116° (decomp.) and 89—91° respectively. Trimethyliodomethylammon-

* In cross references to abstracts, *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

ium iodide when reduced by zinc and acetic acid yielded tetra-methylammonium iodide.   W. G.

Isethionic Acid Derivatives of some Aliphatic Amino-acids. E. SALKOWSKI (*Zeitsch. physiol. Chem.*, 1917, **101**, 1—14. Compare A., 1916, i, 815).—A mixture of equimolecular quantities of the amino-acid and isethionic acid is dissolved in water, heated on the water-bath, and finally at 140—143° for three and a-half to four hours. The cooled mass is dissolved in water, and the product of the reaction precipitated by alcohol. It is then recrystallised from dilute alcohol with the aid of animal charcoal. *Isethionyl-glycine*, $CO_2H \cdot CH_2 \cdot NH \cdot SO_2 \cdot C_2H_4 \cdot OH$, does not melt below 260°; it gives a crystalline *copper* salt. *Isethionylalanine*, $C_5H_{11}O_5NS$, has m. p. 242° (decomp.), and *isethionylleucine*, $C_8H_{17}O_5NS$, m. p. 260° (decomp.). The three compounds have several properties in common; the aqueous solution is acid to litmus, but neutral to Congo-red, unless the solution is very concentrated. Phosphotungstic acid does not produce a precipitate, but only a turbidity, which disappears on warming and reappears on cooling. They reduce ammoniacal silver nitrate and when heated give off sulphur dioxide and a gas, of which the odour resembles that of mercaptan.

A similar compound appears to be formed between isethionic acid and aspartic acid, but it could not be isolated in a crystalline condition.   H. W. B.

Action of Formaldehyde on Glycine and its Metallic Salts. HUGO KRAUSE (*Ber.*, 1918, **51**, 136—150).—The use of formaldehyde in the titration of glycine is now a matter of common knowledge, but no definite work has yet appeared on the nature of the reaction between these compounds, or on the behaviour of the metallic salts of glycine. It is now shown that the salts react like the free amino-acid, and that the products, which may be isolated, in all cases correspond with a condensation product of the formula $C_7H_{14}O_5N_2$. Allowing $C_4H_8O_4N_2$ for two glycine residues, it follows that this product can only be written as
$$OH \cdot CH(CH_2 \cdot NH \cdot CH_2 \cdot CO_2H)_2.$$
From a measurement of the amount of formaldehyde which takes part in the reaction, the very puzzling discovery is made that only one molecule of the aldehyde is required for one of the acid. This is explained by the fact that the methyl alcohol present in the formalin used also enters into the process. If pure formaldehyde solution is used, very little of the compound is formed, relatively much more formaldehyde disappears, and a considerable amount of formic acid is produced. It can be proved, moreover, by a rough quantitative method, that methyl alcohol disappears. The normal reaction is therefore expressed in the equation $2NH_2 \cdot CH_2 \cdot CO_2H + 2CH_2O + CH_3 \cdot OH = C_7H_{14}O_5N_2 + 2H_2O$, whilst the pure aldehyde reacts according to the equation $2NH_2 \cdot CH_2 \cdot CO_2H + 4CH_2O = C_7H_{14}O_5N_2 + H \cdot CO_2H + H_2O$.
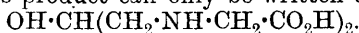
The existence of the $-CH \cdot OH$ group in the molecule is proved by the facts that methyl and ethyl alcohols are formed on heating

the product, that the compound yields an acetate, and that acetone is formed, in traces, by oxidation with chromic acid.

A full account of the isolation of the products is given, and also of the application of the barium salt to the settlement of the above questions. Free *β-hydroxytrimethylenediglycine* is a deliquescent white powder, which decomposes at above 75°, restores the colour of Schiff's reagent, and decomposes alkali carbonates with vigorous effervescence, and its *acetate* is also white. The *sodium* salt, 1H₂O, and *calcium* salt, 2H₂O, are deliquescent powders with alkaline reactions; the *barium* salt, 3H₂O, crystallises in flat rods or leaflets, is not hygroscopic, and is only soluble in 22 parts of water at 18°; the *magnesium* salt, 3H₂O, and an acid *salt*,

$$C_7H_{12}O_5N_2Mg,0{\cdot}25C_7H_{14}O_5N_2,2{\cdot}5H_2O,$$
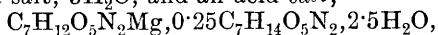
are somewhat hygroscopic; copper glycine gives a fairly insoluble deep blue *salt* of the formula $C_7H_{12}O_5N_2Cu,3H{\cdot}CHO$; with silver glycine, a white precipitate, probably of the normal salt, is formed momentarily, but this soon changes into a yellow *salt*, according to the equation, $C_7H_{12}O_5N_2Ag_2 + 2H_2O = 2OH{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}CO_2Ag + CH_3{\cdot}OH.$ J. C. W.

Action of Ethyl Oxalate on Ethyl β-Aminocrotonate. WILHELM WISLICENUS and KARL SCHÖLLKOPF (*J. pr. Chem.*, 1917, [ii], **96**, 174—179).—The interaction of ethyl oxalate and ethyl β-aminocrotonate in the presence of alcoholic-ethereal potassium ethoxide follows the course stated by Benary, Reiter, and Svenderop (A., 1917, i, 252), the product being the yellow potassium derivative, $CO_2Et{\cdot}C(OK){:}N{\cdot}CMe{:}CH{\cdot}CO_2Et$, of ethyl *N*-ethoxalylaminocrotonate, from which the free ester is liberated on acidifying. In the presence of water, the potassium derivative readily undergoes partial hydrolysis with formation of ethyl β-oxalylaminocrotonate, prisms, which after dehydration have m. p. 106—108°. If ethyl aminocrotonate is allowed to react with a bimolecular proportion of ethyl oxalate and of potassium, a deep yellow dipotassium compound, $C_{12}H_{11}O_7NK_2$, is obtained, probably a cyclic derivative of ethyl *N-C*-diethoxalyl-β-aminocrotonate; on treatment with dilute mineral acid, the aqueous solution of this dipotassium compound deposits yellow needles of a *compound*, $C_{12}H_{12}O_7NK$, containing only one atom of potassium.   D. F. T.

The Nitrogenous Pigments of Molasses. H. FRIEDRICH (*Zeitsch. Zuckerind. Böhm.*, 1917, **41**, 769—771). VL. STANĚK (*ibid.*, 771—773).—Polemical. Friedrich's reply to Staněk's criticism (A., 1917, i, 545), and a rejoinder.   J. C. W.

The Pseudo-system Methyl Thiocyanate, Methylthiocarbimide and Trimethyl Trithiocyanate. J. GILLIS (*Chem. Weekblad*, 1917, **15**, 48—78).—An investigation of the curves of solidification and ebullition of mixtures of methyl thiocyanate and methylthiocarbimide.   A. J. W.

Organo-Cadmium Compounds. I. Simple Cadmium Alkyls. ERICH KRAUSE (*Ber.*, 1917, **50**, 1813—1822).—Cadmium dialkyls can be readily obtained by adding finely powdered, dry

cadmium bromide to ethereal solutions of the magnesium alkyl bromides and distilling the product in a high vacuum. The pure compounds are colourless, highly refractive oils with very unpleasant odours and irritating action on the mucous membrane. The lower members are remarkably volatile, especially in ether vapour, and it is also interesting that the boiling points range higher than those of the corresponding mercury dialkyls. The oils are permanent if stored in tubes filled with pure nitrogen in the dark, but with traces of air and moisture they soon become steely-blue, especially in the light. Cadmium dimethyl merely gets coated with a white crust of the methoxide on exposure to the air, but the others are vigorously oxidised, and even inflame if allowed to fall in drops. The oils sink in water, and then if shaken begin to decompose with a crackling noise, which proceeds for hours. They are mostly stable, in an indifferent atmosphere, up to about 180°, when they decompose so vigorously that part of the liberated metal melts to brilliant drops and another part is deposited as a mirror.

The atomic refraction and dispersion of cadmium in these alkyls rise steadily with the molecular weights, but, taking averages, they are remarkably high compared with the constants for mercury and zinc.

Cadmium dimethyl has m. p. $-4·5°$, b. p. $105·5°/758$ mm., $D_4^{17·9}$ $1·9846$, $n_{H\alpha}$ $1·57766$, n_D $1·58488$, $n_{H\beta}$ $1·60381$, $n_{H\gamma}$ $1·62053$, at $17·9°$. *Cadmium diethyl* has m. p. $-21°$, b. p. $64°/19·5$ mm., $D_4^{18·1}$ $1·6564$, $n_{H\alpha}$ $1·56512$, n_D $1·56798$, $n_{H\beta}$ $1·58447$, $n_{H\gamma}$ $1·59887$, at $18·1°$. *Cadmium di-n-propyl* has m. p. $-83°$, b. p. $84°/21·5$ mm., $D_4^{17·6}$ $1·4201$, $n_{H\alpha}$ $1·52412$, n_D $1·52906$, $n_{H\beta}$ $1·54267$, $n_{H\gamma}$ $1·55452$, at $17·6°$. *Cadmium di-n-butyl* has m. p $-48°$, b. p. $103·5°/12·5$ mm., $D_4^{19·5}$ $1·3056$, $n_{H\alpha}$ $1·51100$, n_D $1·51546$, $n_{H\beta}$ $1·52762$, $n_{H\gamma}$ $1·53793$, at $19·5°$. *Cadmium diisobutyl* has m. p. $-37°$, b. p. $90·5°/20$ mm., D_4^{18} $1·2693$, $n_{H\alpha}$ $1·49528$, n_D $1·49966$, $n_{H\beta}$ $1·51160$, $n_{H\gamma}$ $1·52173$, at $18°$. *Cadmium diisoamyl* has m. p. $-115°$, b. p. $121·5°/15$ mm., D_4^{19} $1·2210$, $n_{H\alpha}$ $1·49967$, n_D $1·50389$, $n_{H\beta}$ $1·51470$, $n_{H\gamma}$ $1·52412$, at $19°$.

All densities are reduced to vacuum standard.   J. C. W.

Some mixed Tin Tetra-alkyls and Tin Trialkyl Haloids.

GERHARD GRÜTTNER and ERICH KRAUSE (*Ber.*, 1917, **50**, 1802—1807).—The physical constants of some twenty known organo-tin compounds are tabulated, and an account is given of about twenty new compounds of the same nature. The material is being gathered for an investigation on the atomic refraction of tin and for studies on compounds containing tin chains (compare following abstract).

Mixed tin tetra-alkyls are prepared by heating tin trialkyl bromides with three times the theoretical quantity of magnesium alkyl haloids, first in ether and then at 100°, and they are converted into the tin trialkyl bromides by the action of bromine at $-40°$ to $-30°$, the rule being that the lightest alkyl group is displaced (compare lead; A., 1917, i, 256). The chlorides are made from the bromides by shaking their ethereal solutions with 33%

sodium hydroxide (or silver hydroxide in the case of the methyl compounds), and then adding hydrochloric acid to the ethereal extract of the tin trialkyl hydroxide.

Tin triethylisobutyl has b. p. 96·5°/17 mm., $D_4^{20\cdot3}$ 1·1390, $n_{H\alpha}$ 1·46977, n_D 1·47304, $n_{H\beta}$ 1·48132; $n_{H\gamma}$ 1·48826, at 20·3°. *Tin dimethyldiisobutyl* has b. p. 85°/16·5 mm., $D_4^{20\cdot1}$ 1·1179, $n_{H\alpha}$ 1·46037, n_D 1·46354, $n_{H\beta}$ 1·47165, $n_{H\gamma}$ 1·47851, at 20·1°. *Tin triethylisoamyl* has b. p. 111°/18·5 mm., $D_4^{20\cdot1}$ 1·1203, $n_{H\alpha}$ 1·46917, n_D 1·47243, $n_{H\beta}$ 1·48050, $n_{H\gamma}$ 1·48739, at 20·1°. *Tin ethyltri*-n-*propyl* has b. p. 117·5/23·5 mm., $D_4^{21\cdot8}$ 1·1225, $n_{H\alpha}$ 1·47053, n_D 1·47374, $n_{H\beta}$ 1·48197, $n_{H\gamma}$ 1·48890, at 21·8°. *Tin diethyldiisobutyl* has b. p. 108·2°/13 mm., $D_4^{20\cdot4}$ 1·1030, $n_{H\alpha}$ 1·47036, n_D 1·47361, $n_{H\beta}$ 1·48167, $n_{H\gamma}$ 1·48846, at 20·4°. *Tin tri*-n-*propylisobutyl* has b. p. 128°/18 mm., $D_4^{24\cdot1}$ 1·0841, $n_{H\alpha}$ 1·46929, n_D 1·47245, $n_{H\beta}$ 1·48042, $n_{H\gamma}$ 1·48711, at 24·1°. *Tin diethyldiisoamyl* has b. p. 131°/13·5 mm., D_4^{19} 1·0725, $n_{H\alpha}$ 1·46957, n_D 1·47268, $n_{H\beta}$ 1·48040, $n_{H\gamma}$ 1·48694, at 19°. *Tin ethyltriisobutyl* has b. p. 125°/16 mm., D_4^{21} 1·0779, $n_{H\alpha}$ 1·47053, n_D 1·47371, $n_{H\beta}$ 1·48167, $n_{H\gamma}$ 1·48830, at 21°. *Tin ethyl*-n-*propyldiisoamyl* has b. p. 141—142°/17 mm., $D_4^{21\cdot9}$ 1·0654, $n_{H\alpha}$ 1·46902, n_D 1·47214, $n_{H\beta}$ 1·47996, $n_{H\gamma}$ 1·48652, at 21·9°. *Tin tetraisobutyl* has m. p. - 13°, b. p. 143°/16·5 mm., D_4^{23} 1·0540, $n_{H\alpha}$ 1·47112, n_D 1·47423, $n_{H\beta}$ 1·48206, $n_{H\gamma}$ 1·48863, at 23°. *Tin triisobutylisoamyl* has b. p. 152·9°/16·5 mm., $D_4^{26\cdot8}$ 1·0356, $n_{H\alpha}$ 1·46851, n_D 1·47174, $n_{H\beta}$ 1·47984, $n_{H\gamma}$ 1·48575, at 26·8°.

Tin diethyl-n-*propyl chloride* has b. p. 108°/17 mm., $D_4^{15\cdot7}$ 1·3848, $n_{H\alpha}$ 1·50207, n_D 1·50580, $n_{H\beta}$ 1·51524, $n_{H\gamma}$ 1·52322, at 15·7°. *Tin diethylisoamyl chloride* has b. p. 125·5—126·5°/13 mm., $D_4^{19\cdot9}$ 1·2994, $n_{H\alpha}$ 1·49443, n_D 1·49805, $n_{H\beta}$ 1·50687, $n_{H\gamma}$ 1·51443, at 19·9°. *Tin diethyl*-n-*propyl bromide* has b. p. 112·2°/16 mm., D_4^{21} 1·5910, $n_{H\alpha}$ 1·51759, n_D 1·52177, $n_{H\beta}$ 1·53232, $n_{H\gamma}$ 1·54129, at 21°. *Tin diethylisobutyl bromide* has b. p. 122°/17 mm., D_4^{20} 1·5108, $n_{H\alpha}$ 1·51194, n_D 1·51586, $n_{H\beta}$ 1·52609, $n_{H\gamma}$ 1·53464, at 20°. *Tin diethylisoamyl bromide* has b. p. 137·5°/17 mm., D_4^{17} 1·4881, $n_{H\alpha}$ 1·51251, n_D 1·51651, $n_{H\beta}$ 1·52653, $n_{H\gamma}$ 1·53503, at 17°. *Tin ethyldiisobutyl bromide* has b. p. 130·6°/13 mm., $D_4^{19\cdot5}$ 1·4085, $n_{H\alpha}$ 1·50452, n_D 1·50837, $n_{H\beta}$ 1·51799, $n_{H\gamma}$ 1·52607, at 19·5°. *Tin ethyldiisoamyl bromide* has b. p. 154—155/16 mm., D_4^{20} 1·3650, $n_{H\alpha}$ 1·50263, n_D 1·50631, $n_{H\beta}$ 1·51562, $n_{H\gamma}$ 1·52347, at 20°

All densities are reduced to vacuum standard, and optical constants at higher temperatures are also recorded in one or two instances.

J. C. W

Hexa-alkyldistannanes. Atomic Linking of Tin. GERHARD GRÜTTNER (*Ber.*, 1917, **50**, 1808—1813).

—Hexa-alkyldistannanes, $R_3Sn\cdot SnR_3$, are prepared by heating tin trialkyl bromides, diluted with an equal volume of ether, with sodium powder at 120°. They are colourless, highly refractive and dispersive liquids with very unpleasant, penetrating odours. They are stable towards heat and are only slowly oxidised on exposure to the air.

Hexaethyldistannane has b. p. 161—162°, $D_4^{17\cdot8}$ 1·3795, $n_{H\alpha}$ 1·53224, n_D 1·53738, $n_{H\beta}$ 1·55065, $n_{H\gamma}$ 1·56210, at 17·8°. *Hexa*-n-*propyldistannane* has b. p. 143·6°/15 mm., $D_4^{19\cdot5}$ 1·2436, $n_{H\alpha}$ 1·52122,

n_D 1·52583, $n_{H\beta}$ 1·53773, $n_{H\gamma}$ 1·54806, at 19·5°. *Hexaisobutyl-distannane* has b. p. 179°/3·5 mm., m. p. 43·8°, D_4^{59} 1·1330. $n_{H\alpha}$ 1·49706, n_D 1·50128, $n_{H\beta}$ 1·51191, $n_{H\gamma}$ 1·52120, at 59°. s.-*Tetra-ethyldi-n-propyldistannane*, $Sn_2Et_4Pr^{\alpha}_2$, has b. p. 165·8°/15 mm., D_4^{20} 1·3313, $n_{H\alpha}$ 1·53042, n_D 1·53541, $n_{H\beta}$ 1·54822, $n_{H\gamma}$ 1·55945, at 15·3°. s.-*Tetraethyldiisobutyldistannane* has b. p. 179°/15·5 mm., $D_4^{19·8}$ 1·2919, $n_{H\alpha}$ 1·52108, n_D 1·52571, $n_{H\beta}$ 1·53772, $n_{H\gamma}$ 1·54815, at 19·8°.

Densities are reduced to vacuum standard.   J. C. W.

Side-chain Chlorine Derivatives of Toluene (Benzyl and Benzylidene Chlorides and Benzotrichloride). H. D. GIBBS and G. A. GEIGER (U.S.-P., 1246739, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 52A).—Gaseous toluene and chlorine are introduced into a suitable reaction chamber in which they are subjected to the action of ultra-violet rays. One mol. of toluene with one, two, or three mols. of chlorine produces benzyl chloride, benzylidene chloride, and benzotrichloride, respectively.   W. P. S.

Bromination of *p*-Nitrotoluene. J. F. BREWSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 406—407).—In view of the usefulness of *p*-nitrobenzyl bromide in the characterisation of acids and phenols (see Reid, A., 1917, i, 333), it is of interest to know that satisfactory yields of the reagent can be obtained by gradually adding bromine dissolved in carbon tetrachloride to a boiling solution of *p*-nitrotoluene, containing a trace of iodine, and exposed to sunlight. [See also *Ind.*, April.]   J. C. W.

Sulphonation of Aromatic Hydrocarbons or their Derivatives. H. BULL (U.S.-P., 1247499, 1917; from *J. Soc. Chem. Ind.*, 1918, **37**, 52A).—The sulphonation is carried out in the presence of an organic solvent of lower specific gravity than sulphuric acid in which the hydrocarbon and sulphonated substance are soluble. The solution of the sulphonated product is removed, and if this is done continuously, the process may be made continuous. The solvent may consist of an excess of the aromatic hydrocarbon.   W. P. S.

Tolane Chlorides from Calcium Carbide, Chlorine, and Benzene. CLINTON DAVIDSON (*J. Amer. Chem Soc.*, 1918, **40**, 397—400).—If powdered calcium carbide, free from iron, is added to cold benzene saturated with chlorine a reaction slowly sets in, the mixture becomes warm, and hydrogen chloride is evolved. After a time, the action subsides, even while much chlorine still remains. If the solution is then chilled, it deposits a mixture of the stable and labile forms of tolane dichloride, but if it is heated for several days until the b. p. rises to 100°, it will then give much tolane tetrachloride. Toluene reacts somewhat more readily, and apparently in the same way.

The mechanism of the process is indicated as follows:
$$CaC_2 + Cl_2 \longrightarrow CCl{:}CCl;$$
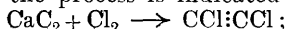
this $+ 2C_6H_6 \longrightarrow$ CPh:CPh, and this $+ Cl_2 \longrightarrow$ CPhCl:CPhCl and CPhCl$_2$·CPhCl$_2$. [See also *Ind.*, April.] J. C. W.

Coloured Condensation Products of Fluorene and Aldehydes. LUIS GUGLIALMELLI and ANGELES DELMON (*Anal. Soc. Quim. Argentina*, 1917, **5**, 124—130. Compare following abstract). —An account of colorations obtained by the action of fluorene in chloroform solution on aliphatic and cyclic aldehydes.
A. J. W.

Chromatic Reactions of Fluorene and Carbohydrates. LUIS GUGLIALMELLI and ANGELES DELMON (*Anal. Soc. Quim. Argentina*, 1917, **5**, 169—176. Compare preceding abstract).— Solutions of fluorene in chloroform and in alcohol give characteristic colour reactions with monoses, polyoses, polyhydric alcohols, and glucosides. A. J. W.

Addition of Ethyl Sodioacetoacetate to the Aromatic Mustard Oils [Thiocarbimides]. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1918, **40**, 415—423).—Ethyl sodioacetoacetate reacts readily with phenyl-, the three tolyl-, *p*-bromophenyl-, and β-naphthyl-thiocarbimides according to the equation
Na·CHAc·CO$_2$Et + R·N:C:S = CH$_3$·CO·CH(CO$_2$Et)·C(SNa):NR.
The products change into thioanilides, NHR·CS·CHAc·CO$_2$Et, on acidifying with hydrochloric acid. In the case of the phenyl, para-substituted phenyl, and naphthyl compounds, these compounds suffer "acid hydrolysis" even with dilute alkali hydroxides, giving the fragments NHR·CS·CH$_2$·CO$_2$H, AcOH, and EtOH, but the *o*- and *m*-tolyl compounds undergo "ketonic hydrolysis," yielding alcohol, carbon dioxide, and the substances CH$_2$Ac·CS·NH·C$_6$H$_4$Me. Ethyl and benzyl derivatives of ethyl sodioacetoacetate react with phenylthiocarbimide less readily, and the products are more stable towards alkalis.
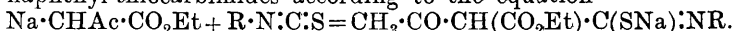
Ethyl sodioacetoacetate, obviously prepared in a non-hydroxylic solvent (ether), and phenylthiocarbimide yield *ethyl acetylthionmalonanilate*, NHPh·CS·CHAc·CO$_2$Et, which crystallises in pale yellow, prismatic needles, m. p. 82—83°, yields hydrogen sulphide, ethyl acetate, and aniline hydrochloride when boiled with concentrated hydrochloric acid, and silver sulphide and acetaldehyde with warm silver nitrate, and changes into malonthionanilic acid, NHPh·CS·CH$_2$·CO$_2$H (Ruhemann, T., 1908, **93**, 624), on warming with sodium hydroxide.

o-Tolylthiocarbimide yields such an unstable primary product that it cannot be isolated. Ketonic hydrolysis takes place so readily that the product is *acetothionaceto-o-toluidide*,
COMe·CH$_2$·CS·NH·C$_6$H$_4$Me,
which crystallises in nearly colourless needles, m. p. 73—75°, and is hydrolysed by concentrated hydrochloric acid to acetic acid and Wallach's thionaceto-*o*-toluidide, CH$_3$·CS·NH·C$_6$H$_4$Me (the m. p. is
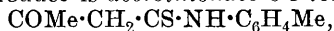
now given as 91—92° instead of 67—68°). *Acetothionaceto*-m-*toluidide* has m. p. 83—84°. *p*-Tolylthiocarbimide gives *ethyl acetylthionmalon*-p-*toluidate*, glistening, diamond-shaped tablets, m. p. 81° (the primary *sodium* derivative has m. p. 61—62°), and this yields *thionmalon*-p-*toluidic acid* on hydrolysis, in long, flat needles which melt at 97°, and change thereby into thionaceto-*p*-toluidide, m. p. 129·5—130·5° (Wallach).

Ethyl acetylthionmalon-p-*bromoanilate* has m. p. 81—83°; *thionmalon*-p-*bromoanilic acid* forms cream-coloured, flat needles and plates, and changes at 150° into p-*bromothionacetanilide*, which crystallises in narrow, hexagonal plates, m. p. 153°.

Ethyl acetylthionmalon-β-*naphthylamate*,

$$C_{10}H_7 \cdot CS \cdot CHAc \cdot CO_2Et$$
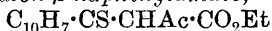
(not purified), yields *thionmalon*-β-*naphthylamic acid*, in pale yellow plates, m. p. 87—89° (decomp.).

Ethyl sodio-α-ethylacetoacetate gives *ethyl α-acetyl-α-ethyl-thionmalonanilate* as an oil, which is much more stable towards acids and alkalis than the above analogues. Ethyl sodio-α-benzyl-acetoacetate reacts very sluggishly with phenylthiocarbimide, and the only product described is a *polymeride* of, apparently, β-phenyl-thionpropionanilide, $CH_2Ph \cdot CH_2 \cdot CS \cdot NHPh$, having m. p. 222—223° (decomp.).   J. C. W.

Unsaturated Groups in Chemical and Pharmacological Connexions. I. J. von Braun and Z. Köhler (*Ber.*, 1918, **51**, 79—96).—That the unsaturated radicle, allyl, differs in many respects from aliphatic radicles is well known. Chemically, the most striking differences are to be found in its weaker attachments to nitrogen (compare Collie and Schryver, T., 1890, **57**, 767; von Braun, A., 1900, i, 641; Komatsu, A., 1913, i, 39), halogens (Clarke, T., 1910, **97**, 416; von Braun, A., 1912, i, 433), and oxygen (Claisen and Eisleb, A., 1913, i, 1175). Pharmacologically, it is a striking fact that by the replacement of an *N*-methyl group by allyl in choline or codeine, bases are obtained which are antagonistic to the parent bases (A., 1917, i, 254; 1916, i, 665).

The question naturally arises, are these effects peculiar to allyl or are they reproduced by other unsaturated radicles, and, if so, is the position of the ethylene linking of moment? The problem has therefore been attacked, and so far the chemical influences of the cinnamyl, $-CH_2 \cdot CH{:}CHPh$, the 2-furfuryl, $-CH_2 \cdot C{<}^{O-CH}_{CH \cdot CH}$,
and Δ⁵-pentenyl, $-CH_2 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$, groups have been examined. It is found that the last resembles saturated radicles in its attachments, whilst the first two resemble allyl. An ethylene linking between the β- and γ-carbon atoms is therefore one factor of importance.

I. The Cinnamyl Radicle.—Cinnamyl bromide is conveniently prepared by heating cinnamyl alcohol with three times its weight of hydrobromic acid (D 1·48). The halogen is so loosely combined that it is quickly removed by warm water alone. The bromide

combines most readily with tertiary bases; for its behaviour with pyridine, see Clarke (*loc. cit.*); with trimethylamine, it forms *cinnamyltrimethylammonium bromide*, in silvery leaflets, m. p. 165°. It reacts vigorously with magnesium, the bromine being removed and $a\zeta$-diphenyl-$\Delta^{a\epsilon}$-hexadiene formed. With magnesium ethyl iodide, it yields this diphenylhexadiene and also *a-phenyl-Δ^{a}-pentene*, b. p. 202—205°, D_4^{22} 0·8782, n_D^{20} 1·51575. It condenses with dimethylamine to form *cinnamyldimethylamine*,

$$NMe_2 \cdot CH_2 \cdot CH : CHPh,$$
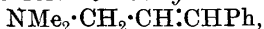
as a colourless liquid with strong basic odour, b. p. 100—101°/7 mm., which forms a *picrate*, m. p. 110°.

II. THE 2-FURFURYL RADICLE.—Furfuraldehyde is converted by Schwabbauer's method (A., 1902, i, 230) into 2-furfurylmethylamine, b. p. 59—60°/25 mm., which forms a *benzoyl* derivative, b. p. 180—185°/5 mm., and reacts with ethyl iodide to give

2-furfurylmethylethylamine, $NMeEt \cdot CH_2 \cdot C \!\!<\!\! \begin{smallmatrix} O \text{---} CH \\ CH \cdot CH \end{smallmatrix}$. This is a

colourless base which smells strongly like ammonia, has b. p. 69—70°/23 mm., forms a *picrate*, m. p. 91°, a *platinichloride*, m. p. 147°, and a *methiodide*, m. p. 101°, and reacts very vigorously with cyanogen bromide to give some *di-2-furfurylmethylethylammonium bromide*, $(C_4H_3O \cdot CH_2)_2NMeEtBr$, m. p. 151°, a little methylethylcyanamide, $CN \cdot NMeEt$, but also, in 80% yield, the desired *2-furfuryl bromide*. This is a very unstable oil, which severely attacks the mucous membrane, the skin, rubber, and cork, is quickly hydrolysed by warm water, and energetically combines with tertiary amines. *2-Furfuryltrimethylammonium platinichloride*, m. p. 146—148° (decomp.), is mentioned in this connexion.

2-Furfurylmethylamine combines with ethylene oxide at 50° to form *2-furfurylmethyl-β-hydroxyethylamine*,

$$C_4H_3O \cdot CH_2 \cdot NMe \cdot CH_2 \cdot CH_2 \cdot OH,$$
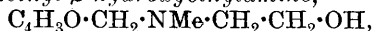
as a glycerol-like liquid, b. p. 105°/6 mm., which yields a *picrate*, m. p. 68—70°, a very soluble *aurichloride*, a *platinichloride*, decomp. 133°, and a *methiodide*, m. p. 77—80°.

III. THE Δ^{δ}-PENTENYL RADICLE.—The parent substance in this series is the dimethylpentenylamine, $CH_2 : CH \cdot [CH_2]_3 \cdot NMe_2$, which is obtained by the Hofmann degradation of piperidine. This reacts very vigorously with cyanogen bromide, about half of the base being converted into its methobromide, and the remainder into *methyl-Δ^{δ}-pentenylcyanamide*, $CH_2 : CH \cdot C_3H_6 \cdot NMe \cdot CN$, b. p. 96—98°/7 mm. This is hydrolysed by boiling with 25% sulphuric acid to *methyl-Δ^{δ}-pentenylamine*, a mobile liquid, b. p. 107—109°, which fumes in the air, and forms a *platinichloride*, m. p. 158°, a *picrate*, m. p. 150°, and a *benzoyl* derivative, b. p. 164—167°/7 mm. This amide, $CH_2 : CH \cdot C_3H_6 \cdot NMeBz$, gives the desired Δ^{δ}-pentenyl haloids on fusion with phosphorus pentahaloids, but the yields are very small. Another attempt to prepare the haloids was therefore made.

A solution of sodium amyloxide is cautiously warmed with

αε-dichloropentane, when the di-ether, $C_5H_{10}(O \cdot C_5H_{11})_2$ (Hamonet, A., 1904, i, 705), and ε-*chlorodiamyl ether*, $C_5H_{11} \cdot O \cdot C_5H_{10}Cl$, are formed, the yield of the latter being 40%. This ether is a colourless, pleasant-smelling liquid, b. p. 100—105°/8 mm., which reacts with dimethylamine to form *dimethylamyloxyamylamine*, as a limpid liquid with penetrating odour, b. p. 99—103°/7 mm. [The amyloxy-residue in these compounds is derived from ordinary amyl alcohol; the prefix "g.-" is proposed, from Gärung = fermentation, to signify this.] The tertiary amine is hydrolysed by means of concentrated hydrochloric acid to *dimethyl-ε-chloroamylamine hydrochloride*, which is snow-white, and may be converted into the *aurichloride*, m. p. 64—65°. The free base is stable enough to be transformed into the *methiodide*, $C_5H_{10}Cl \cdot NMe_3I$, m. p. 134°, but this loses some chlorine as well as the iodine on treatment with silver oxide, so that on distilling the quaternary ammonium hydroxide only an impure specimen of the desired pentenyl chloride can be obtained.

The purest specimen of Δ^δ-*pentenyl bromide* so far obtained had b. p. 110°. It has a sweet odour, does not attack the eyes, is not readily attacked by water, does not combine easily with tertiary amines, but reacts fairly completely with magnesium, in all these respects differing from allyl bromide. Not sufficient magnesium Δ^ϵ-pentenyl bromide could be obtained in this way for any experiments, but the compound was prepared from αδε-tribromopentane, as follows.

ε-Phenoxyamyl iodide is treated with trimethylamine, the quaternary iodide is converted into the hydroxide, and this is distilled, when a 40% yield of ε-*phenoxy-Δ^α-pentene* is obtained as a pleasant-smelling, limpid liquid, b. p. 109—111°/13 mm., D_4^{20} 0.9464, n_D^{20} 1.50. The *dibromide* of this, b. p. 190—205°/12 mm., is hydrolysed by prolonged boiling with fuming hydrobromic acid to αδε-*tribromopentane*, which is a heavy oil, b. p. 128—132°/11 mm., with spicy odour. This behaves like other tribromides which contain two bromine atoms attached to neighbouring carbon atoms when treated with magnesium (A., 1911, i, 701, 938), the chief product being magnesium Δ^δ-pentenyl bromide, $CH_2{:}CH \cdot C_3H_6 \cdot MgBr$. This is proved by the fact that Δ^δ-hexenoic acid, $CH_2{:}CH \cdot C_3H_6 \cdot CO_2H$, is produced from it by the action of carbon dioxide (compare Fichter and Langguth, A., 1897, i, 590).

                                                                    J. C. W.

Dicyclohexylamine.   Solid   Hydrate   and   Alcoholate. Gustave Fouque (*Compt. rend.*, 1918, **166**, 394—395).—Dicyclohexylamine, when poured on to water at below 23°, gave a crystalline *hydrate*, $NH(C_6H_{11})_2,H_2O$, m. p. 23°. The solubility of the amine in water, and of water in the amine, diminished as the temperature rose above 23°. An equimolecular mixture of dicyclohexylamine and ethyl alcohol at the ordinary temperature gave the *alcoholate*, $NH(C_6H_{11})_2,EtOH$, m. p. 28°, which dissociated in the air.   W. G.

Oxalyl Chloride as a Reagent in Organic Chemistry. II. Preparation of Aromatic Anhydrides. Reaction with Alcohols. ROGER ADAMS, W. V. WIRTH, and H. E. FRENCH (*J. Amer. Chem. Soc.*, 1918, **40**, 424—431. Compare A., 1916, i, 140; 1917, i, 4).—When slightly more than one molecular proportion of oxalyl chloride is added to a boiling solution of two parts of an aromatic acid in benzene, very good yields of the acid anhydride are obtained. The reaction apparently proceeds in two stages, thus: $2R \cdot CO_2H + C_2O_2Cl_2 = 2HCl + (R \cdot CO \cdot O)_2C_2O_2$, and this $= (R \cdot CO)_2O + CO + CO_2$, for *m*-nitro-, 2:4- and 3:5-dinitro-benzoic acids yield the intermediate mixed anhydrides (probably owing to the .insolubility of these in benzene), which decompose in the indicated way on heating or on treatment with cold pyridine.

The advantages of the method are obvious. The following anhydrides have been prepared in this way: benzoic; the three toluic; o-*chlorobenzoic*, white, prismatic needles, m. p. 78—79°; m-*chlorobenzoic*, short, white needles, m. p. 95°; *p*-chlorobenzoic; m-*iodobenzoic*, plates, m. p. 134°; o-nitrobenzoic; m-*nitrobenzoic oxalic anhydride*, $(NO_2 \cdot C_6H_4 \cdot CO \cdot O)_2C_2O_2$, pale yellow, decomposing at 157° into m-*nitrobenzoic anhydride*, m. p. 163° [Autenrieth's anhydride, m. p. 47° (A., 1901, i, 186), was really Greene's *m*-nitrobenzoic acetic anhydride, $Ac \cdot O \cdot CO \cdot C_6H_4 \cdot NO_2$ (A., 1890, 53)]; 3:5-*dinitrobenzoic oxalic anhydride*, decomp. 175°, and 3:5-*dinitrobenzoic anhydride*, m. p. 109°; 2:4-*dinitrobenzoic oxalic anhydride*, m. p. 205—209° (decomp.), and 2:4-*dinitrobenzoic anhydride*, m. p. 160°.

Just as phenols react with oxalyl chloride in the presence of pyridine, at 0°, to form oxalates, so primary and secondary alcohols give these esters in 50% yield, on an average. Tertiary alcohols usually do not react at all. The following *oxalates* have been prepared by this method: *benzhydryl*, m. p. 142—143°; *phenyl-o-tolylcarbinyl*, $(CHPh \cdot C_6H_4Me)_2C_2O_4$, m. p. 86—87°; *benzoin oxalate*, $(COPh \cdot CHPh)_2C_2O_4$, m. p. 243—245°; *piperonoin oxalate*, $C_{34}H_{26}O_8$, m. p. 225—226°; bornyl; menthyl; *iso*propyl; and *diphenylmethylcarbinyl oxalate*, $(CMePh_2)_2C_2O_4$, pyramids, decomp. 170—185° (yield very small). [See also *Ind.*, April.]

J. C. W.

Preparation of Solutions of Glycol Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 298185, 1915; from *Chem. Zentr.*, 1917, ii, 145).—Ethylene glycol monobenzoate, m. p. 45°, can be dissolved in almost any proportion in solutions of the alkali salts of benzoic, toluic, salicylic, or cresotic acid; in place of the benzoyl derivative of ethylene glycol, the corresponding *m*- and *p*-toluoyl, o-chlorobenzoyl, or salicyl compound may be used.

D. F. T.

Preparation of Acyl Derivatives of Aromatic Amides. MENDEL PERELSTEIN and EMIL BÜRGI (D.R.-P., 297875, 1915; from *Chem. Zentr.*, 1917, ii, 144—145).—By introducing the *iso*valeryl radicle into the amino-group of aromatic amides, compounds are

obtained possessing the soporific power of the amides, but much less poisonous. The method of preparation is by the direct interaction of the *iso*valeryl haloid with the acid amide, either in the molten condition or dissolved in an organic solvent in the presence of a dehydrating agent. By brominating the *iso*valeryl-substituted amide or by using an α-bromo*iso*valeryl haloid for the first reaction, it is possible to produce compounds of especial therapeutic value. The following substances were obtained: *cinnamoyl-α-bromo*isovalerylamide*, colourless needles, m. p. 118° (*dibromide*, crystals, m. p. 145° with reddening); *benzoyl-α-bromo*isovaleryl-amide*, colourless needles, m. p. 142—143°; *bis-α-bromo*isovaleryl-salicylamide* [*α-bromo*isovaleroxybenzoyl-α-bromo*isovalerylamide*], needles, m. p. 119°; *benzoyl*isovalerylamide*, needles, m. p. 89°; *cinnamoyl*isovalerylamide*, needles, m. p. 103° (*dibromide*, m. p. 165°).   D. F. T.

The Walden Inversion. VI. Influence of the Solvent on the Sign of the Product in the Conversion of Phenylbromoacetic Acid into Phenylaminoacetic Acid. GEORGE SENTER and STANLEY HORWOOD TUCKER (T., 1918, **113**, 140—151; compare A., 1915, i, 535; 1916, i, 815; 1917, ii, 301).—It was found in the first experiments of this series that the sign of the amino-acid obtained by the action of ammonia on active phenylchloroacetic acid depends on the nature of the solvent employed, and it appeared to be of interest to examine this phenomenon in other cases.

Experiments on the displacement of bromine by the amino-group in the case of *l*-phenylbromoacetic acid have given the following results: (*a*) in aqueous solution, or in the higher alcohols (*n*-butyl, trimethylcarbinol, *n*-heptyl), the amino-acid obtained is opposite in sign, which agrees with the behaviour of phenylchloroacetic acid; (*b*) in the lower alcohols (methyl, ethyl, *n*- and *iso*-propyl) the product is also opposite in sign, whereas the amino-acid obtained from phenylchloroacetic acid in these solvents has the same sign as the parent halogeno-acid; (*c*) in acetonitrile or liquid ammonia, the product has the same sign, as in the earlier case; (*d*) considerable racemisation takes place in the lower alcohols, but not in the higher; (*e*) the presence of ammonium bromide has little racemising influence in aqueous solution, but considerable in liquid ammonia; (*f*) small quantities of iminodiphenyldiacetic acid, of high activity, opposite in sign to the original acid, are formed in all solvents.

The mechanism of the formation of the imino-acid is discussed. It is probable that it is formed by the direct action of ammonia on two molecules of the halogeno-acid, rather than by the interaction of the halogeno-acid with the amino-acid.   J. C. W.

The Walden Inversion. VII. Influence of the Solvent on the Sign of the Product in the Conversion of α-Bromo-β-phenylpropionic Acid to α-Amino-β-phenylpropionic Acid (Phenylalanine). Iminodiphenyldipropionic Acid. GEORGE SENTER, HARRY DUGALD KEITH DREW, and GERALD HARGRAVE MARTIN (T., 1918, **113**, 151—163).—α-Bromo-β-phenylpropionic

acid has been examined in this series as the phenyl group is removed from the asymmetric carbon atom, and consequently different results might perhaps be anticipated. It is found that in all the solvents tried, water, alcohols, and even acetonitrile and liquid ammonia, the amino-acid has the opposite sign to the parent active acid, although very considerable racemisation occurs in the last two media. The most remarkable difference between this case and the earlier ones is, however, that ammonium bromide actually lessens racemisation when the reaction is carried out in liquid ammonia.

α-*Imino*-$\beta\beta$-*diphenyldipropionic acid*, $NH[CH(CH_2Ph)\cdot CO_2H]_2$, is formed in small amounts in all the solvents, with the same sign as the bromo-acid.

The perplexing differences observed in the three cases (papers V., VI., and VII.) are perhaps best accounted for on the assumption that the action of ammonia on the halogeno-acids proceeds as two simultaneous reactions, the formation of both d- and l-aminoacids. Which of these reactions predominates depends on the nature of the acid, the nature of the solvent, and other factors.

[For experimental details, see the original.] J. C. W.

Preparation of a Solid *iso*Valeric Acid Compound Soluble in Water. HUGO VOSWINCKEL (D.R.-P., 294877, 1914; from *Chem. Zentr.*, 1917, ii, 144).—By warming a mixture of *iso*valeryl chloride and mandelic acid in benzene solution, iso*valerylmandelic* [α-iso*valeryloxyphenylacetic*] *acid*,

$$C_4H_9\cdot CO\cdot O\cdot CHPh\cdot CO_2H,$$
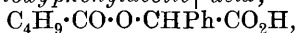
hard crystals, m. p. 71°, is obtained, the *calcium* salt of which is a granular solid soluble in water. D. F. T.

Phthalic Acid Derivatives : Constitution and Colour. V. Some Derivatives of Tetrachloro- and Tetraiodo-phthalimides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 198—214. Compare A., 1914, i, 415; 1915, i, 686, 692).—In the hope of obtaining a clearer insight into the relationship between the absorption bands shown by various members of the same family and a more exact knowledge of the origin of each band, investigation is being made of the absorption spectra of a large number of compounds related to phthalic acid, each differing only slightly from its neighbours. The present paper only deals with the preparation of phthalic acid derivatives in which halogen is substituted into the benzene ring, or in which the anhydride oxygen is replaced.

Tetrachlorophthalic anhydride, prepared by the action of chlorine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine, gives unstable, deeply coloured additive compounds with certain amines; with dimethylaniline and dimethyl-p-toluidine the *additive* compounds were isolated as red prisms, $C_8O_3Cl_4,NPhMe_2$, and almost purple crystals,

$$C_8O_3Cl_4,C_7H_7\cdot NMe_2,$$
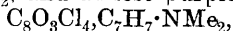
respectively, but the formation of similar compounds with diethylamine, methylaniline, and the two naphthylamines could only be

detected by the red colour of mixtures of the anhydride and the respective bases, dissolved in xylene if necessary; diphenylamine and aniline yielded yellow solutions, whilst no colour change was observed with pyridine and triethylamine; the presence of chlorine is not essential to this reaction because 3-nitrophthalic anhydride and other substituted phthalic anhydrides, including, indeed, even phthalic anhydride itself, are capable of similar behaviour, the effect being so general as to suggest that the formation of such additive compounds is an essential first stage in the condensation of phthalic anhydride and its nuclear substituted derivatives with aromatic amines. In these additive compounds it is believed that the attachment between the two molecules occurs by means of residual valency at the anhydride oxygen atom and the nitrogen atom of the amine; with a tertiary amine no further change is possible, but with a secondary amine rearrangement subsequently occurs with formation of the colourless salt, whilst with a primary amine, such as aniline, the formation of the aniline phthalanilate can be succeeded by loss of aniline and production of the anil. In accordance with this view, the yellow solution of tetrachlorophthalic anhydride and aniline in benzene gradually deposits *aniline tetrachlorophthalanilate*, $C_{20}H_{14}O_3N_2Cl_4$, a colourless, crystalline powder, m. p. 271—273° (corr.), which readily undergoes further condensation to tetrachlorophthalanil, m. p. 274—275° (corr.). When tetrachlorophthalic anhydride is heated with aniline, preferably in an inactive atmosphere, the reaction goes still further with production of 3-*anilino*-4 : 5 : 6-*trichlorophthalanil*, $C_{20}H_{11}O_2N_2Cl_3$, orange blades, m. p. 179·5—180·5° (corr.), and a *dianilinodichlorophthalanil*, $C_{26}H_{17}O_2N_3Cl_2$, bright, scarlet blades, m. p. 182·5—183·5° (corr.). *Tetrachlorophthal-o-tolil*, $C_{15}H_7O_2NCl_4$, colourless, rhombic leaflets, m. p. 232—236·5° (corr.), also its meta-*isomeride*, m. p. 245·5—246·5° (corr.), and para-*isomeride*, were obtained by heating a solution of tetrachlorophthalic anhydride and the corresponding toluidine in acetic acid. Tetrachlorophthal-*o*-tolil exhibits dimorphism, separating from acetic acid or alcohol in colourless, hexagonal leaflets, which at 207° (corr.) soften and become yellow with formation of a coloured modification, m. p. 214—214·5° (corr.); this is stable only above 118°, and can also be obtained in long, hair-like crystals by seeding the warm solution of the ordinary form in acetic acid or alcohol with a little of the yellow form. In accordance with the probability that the yellow form below its transition point must possess more free energy than the colourless modification, it is found that the former yields coloured *additive* compounds with benzene (3 or $4C_{15}H_7O_2NCl_4,C_6H_6$, long, yellow, hair-like crystals), *m*-xylene ($4C_{15}H_7O_2NCl_4,C_6H_4Me_2$), nitrobenzene ($4C_{15}H_7O_2NCl_4,C_6H_5\cdot NO_2$, yellow blades), and dimethylaniline ($5C_{15}H_7O_2NCl_4,NMe_2Ph$, scarlet needles), whereas the colourless variety shows no such tendency. The following anils were obtained by heating together the corresponding base and tetrachlorophthalic anhydride in acetic acid solution : *tetrachlorophthal-o-nitroanil*, $C_{14}H_4O_4N_2Cl_4$, colourless

leaflets, m. p. 272—$273°$ (corr.); *tetrachlorophthal*-m-*nitroanil*, colourless blades, m. p. 300—$301\cdot5°$ (corr.); *tetrachlorophthal*-p-*nitroanil*, fine, colourless needles, m. p. 292—$297°$ (corr.); *tetrachlorophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NCl_4$, bright yellow needles, m. p. 305—$307°$ (corr.); *tetrachlorophthal*-p-*acetylaminoanil*, pale yellow nodules or colourless needles, m. p. near $339°$ (corr.).

For the preparation of tetrachlorophthalimide, m. p. 338—$339°$ (corr.), Graebe's method (*Annalen*, 1887, **238**, 332) is less convenient than one employing formamide in place of ammonia, a warm solution of the tetrachlorophthalic anhydride in the former rapidly depositing the imide. In a similar manner tetra-iodophthalic anhydride reacts with formamide, giving *tetraiodophthalimide*, $C_8HO_2NI_4$, fine, yellow needles, m. p. 370—$380°$ (decomp.), whilst condensation of the anhydride with the various aromatic amines in nitrobenzene solution gives *tetraiodophthalanil*, $C_{14}H_5O_2NI_4$, yellow blades, m. p. 314—$315°$ (corr.); *tetraiodophthal-o-tolil*, $C_{15}H_7O_2NI_4$, minute, yellow crystals, m. p. 314—$315°$ (corr.); *tetraiodophthal*-m-*tolil*, yellow blades, m. p. 325—$326°$; *tetraiodophthal*-p-*tolil*, yellow blades, m. p. 317—$318°$ (corr.); *tetraiodophthal*-m-*nitroanil*, $C_{14}H_4O_4N_2I_4$, yellow, matted needles, m. p. 318—$319°$ (corr.); *tetraiodophthal*-p-*hydroxyanil*, $C_{14}H_5O_3NI_4$, fine, yellow needles, m. p. 330—$336°$ (corr.), and *tetraiodophthal*-p-*acetylaminoanil*, minute, yellow blades, m. p. $339°$ (corr., decomp.). D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VI. Action of Amines on Dichlorophthalic Anhydrides. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 214—218. Compare preceding abstract).—3 : 4-Dichlorophthalic acid reacts with aniline in boiling acetic acid solution, yielding 3 : 4-*dichlorophthalanil*, $C_{14}H_7O_2NCl_2$, which usually crystallises in very pale yellow, silky needles, m. p. $174°$ (corr.), but on account of the readiness of transformation into a second modification, colourless prisms, m. p. 182—$182\cdot5°$ (corr.), the lower m. p. can be observed only by sudden immersion of a small quantity of the needles in a bath near $174°$. When heated with an excess of aniline in an inert atmosphere, the dichlorophthalic acid undergoes further conversion into 3-*anilino-4-chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, orange leaflets, m. p. $159\cdot5$—$160°$. In a similar manner, 3 : 6-dichlorophthalic acid is convertible into 3 : 6-dichlorophthalanil, m. p. 197—$198°$ (corr.), and 3-*anilino-6-chlorophthalanil*, $C_{20}H_{13}O_2N_2Cl$, which exhibits dimorphism, the crystals commonly obtained from alcohol forming orange needles, which on rapid heating have m. p. $141°$ (corr.), whereas on slow heating or on being kept in contact with the solvent the substance becomes changed into a second form, small, orange prisms, m. p. 160—$160\cdot5°$. 4 : 5-Dichlorophthalic anhydride reacts with aniline in boiling acetic acid, yielding 4 : 5-*dichlorophthalanil*, colourless. rhombic leaflets, m. p. $212\cdot5$—$213°$ (corr.), but shows no tendency to the further replacement of chlorine by the anilino-group. D. F. T.

Phthalic Acid Derivatives: Constitution and Colour. VII. Di-iodo-, Tri-iodo-, and Dichloroiodo-phthalic Acids. DAVID S. PRATT and GRANVILLE A. PERKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 219—236. Compare preceding abstracts).—In extension of the investigation in which chlorine in halogenated phthalanils was observed to be replaceable by the anilino-group, various iodo-phthalic acids were prepared for interaction with aniline.

When phthalic anhydride dissolved in fuming sulphuric acid is treated with iodine the composition of the product is dependent on the temperature; prolonged heating at 75° gives rise to nearly equal amounts of the 3:4- and 3:6-di-iodo-acids with much smaller quantities of 4:5-di-iodophthalic acid and 3:4:6-tri-iodophthalic anhydride, whereas the product obtained on rapid heating to 200° contains approximately the same amount of the 4:5-di-iodo-acid with a larger amount of the 3:4-di-iodo-acid and the tri-iodo-anhydride at the expense of the 3:6-di-iodo-acid. Traces of 4-iodo-phthalic acid and tetra-iodophthalic anhydride were also observed. A partial separation of the products is possible by esterification, only the 4:5-di-iodo-acid and part of the 3:4-di-iodo-acid forming normal esters with alcohol and hydrogen chloride. Separation was finally effected, however, by fractional precipitation from a solution of the disodium salts with acetic acid, causing deposition of the monosodium salts in the order 4:5-di-iodo-acid, tri-iodo-acid, and 3:4-di-iodo-acid, the salt of the 3:6-di-iodo-acid remaining in solution, aided by the knowledge that on recrystallisation from acetic acid the 3:4- and 4:5-di-iodo-acids separate unchanged, whereas the 3:6-di-iodo-acid and the tri-iodo-acid become converted into the corresponding anhydrides, which are very soluble in benzene. The structure of the various acids was determined by heating with sodium hydroxide solution and examination of the resulting hydroxy-acids. The dichlorophthalic anhydrides can be iodinated in a similar manner to the parent phthalic anhydride.

3:4-*Di-iodophthalic acid*, $C_8H_4O_4I_2$, colourless leaflets, m. p. 212—213° (corr.), when heated with acetic anhydride in benzene solution, yields the corresponding *anhydride*, $C_8H_2O_3I_2$, almost colourless prisms, m. p. 198—198·5° (corr.), is slowly hydrolysed by sodium hydroxide solution with formation of 3:4-dihydroxybenzoic acid, and reacts with aniline in boiling acetic acid, forming an *anil*, $C_{14}H_7O_2NI_2$, very pale yellow prisms, m. p. 270—271° (corr.).

3:6-*Di-iodophthalic acid* forms colourless leaflets which undergo gradual dehydration even below 100° with formation of the *anhydride*, colourless prisms, m. p. 234·5—235·5° (corr.). When heated with aqueous sodium hydroxide, 3-hydroxyphthalic acid is produced with much tarry matter, but no 3:6-dihydroxy-acid; however, by boiling a solution of the anhydride with aqueous pyridine and silver sulphate it is possible to obtain 6-*iodo*-3-*hydroxyphthalic anhydride* (*acetate*, $C_{10}H_5O_5I$, square crystals, m. p. 148·5—152·5°, corr.). which is hydrolysable with concentrated sodium hydroxide solution to 3:6-dihydroxyphthalic acid. 3-Hydroxyphthalic acid, $C_8H_6O_4$, colourless prisms, m. p. 161—163° (corr.; decomp.), readily passes into the anhydride, orange-yellow crystals, m. p. 198—199° (corr.;

Jacobsen, A., 1883, 1124, gives 145—148°), the *acetate* of which crystallises in colourless leaflets, m. p. 113·5—115·5° (corr.), and the *benzoate* in leaflets, m. p. 147·5—148° (corr.). 3 : 6-Di-iodophthalanil, prepared similarly to its 3 : 4-isomeride, forms colourless, rectangular plates, m. p. 233·5—234° (corr.).

4 : 5-*Di-iodophthalic acid*, colourless needles (probably with acetic acid of crystallisation) or leaflets, m. p. 221—222° (corr.; decomp.), on dehydration with acetic anhydride or by mere heating is converted into the *anhydride*, colourless prisms, m. p. 216·5—217° (corr.); hydrolysis of the acid with sodium hydroxide yields 4 : 5-dihydroxyphthalic acid and perhaps a little 3 : 4 : 5-trihydroxyphthalic acid. 4 : 5-*Di-iodophthalanil*, prepared by heating the acid with acetic anhydride and aniline in acetic acid solution, exhibits dimorphism, separating from acetic acid or xylene in pale yellow needles, which on rapid heating have m. p. 231·5—233° (corr.), but on gradual heating undergo transformation into a modification, m. p. 241·5—243° (corr.), the latter being also obtained in the form of pale yellow, hexagonal leaflets from the molten anil on very slow cooling.

3 : 4 : 6-*Tri-iodophthalic anhydride*, $C_8HO_3I_3$, bright yellow, rhombic pyramids, m. p. 230—231° (corr.), yields an *anil*, $C_{14}H_6O_2NI_3$, light yellow, microscopic needles, m. p. 254·5—255·5° (corr.), and on hydrolysis with sodium hydroxide gives a mixture of 3 : 6-dihydroxyphthalic acid with other substances, probably including a little 3 : 5-dihydroxybenzoic acid.

3 : 4-*Dichloro*-5 : 6-*di-iodophthalic anhydride*, $C_8O_3Cl_2I_2$, yellow prisms, m. p. 229·5—230·5° (corr.), obtained by the interaction of 3 : 4-dichlorophthalic anhydride and iodine in heated fuming sulphuric acid, yields an *anil*, $C_{14}H_5O_2NCl_2I_2$, pale yellow needles, m p. 242·5—243·5° (corr.). 3 : 6-*Dichloro*-4 : 5-*di-iodophthalic anhydride*, yellow prisms, m. p. 258—258·5° (corr.), obtained in a similar manner, yields an *anil*, pale yellow needles, m. p. 232—232·5° (corr.). 4 : 5′-*Dichloro*-3 : 6-*di-iodophthalic anhydride*, yellow blades, m. p. 232—233·5° (corr.), forms an *anil*, very pale yellow needles, m. p. 282·5—284° (corr.), and when heated with excess of aniline for twenty-four hours at 130° undergoes further conversion into 4 : 5-*dichloro*-3 : 6-*dianilinophthalanil*,

$$C_{26}H_{17}O_2N_3Cl_2,$$

orange-red crystals, m. p. 181·5—185° (corr.), quite distinct from the isomeric product obtained by the action of aniline on tetrachlorophthalanil (this vol., i, 168). D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XII. Tetrachlorophthaloxime and some of its Derivatives. DAVID S. PRATT and CHARLOTTE H. MILLER (*J. Amer. Chem. Soc.*, 1918, **40**, 407—412. Compare preceding abstracts).—Unsubstituted phthaloxime exists in two chromoisomeric forms (A., 1912, i, 190), but only one colour has been observed with the tetrachloro- and tetraiodo-phthaloximes and their ethers and esters. The ethers of tetrachlorophthaloxime, however, often exist in two modifications,

usually cotton-like masses and stable, stout prisms, which are inter-changeable, and this dimorphism has not been observed in the other series.

Tetrachlorophthaloxime (A., 1913, i, 100) forms a red *silver* salt, from which the following colourless ethers,

$$C_6Cl_4 \diagdown{}^{CO\text{------}}_{C(:N\cdot OR)} \diagup O,$$
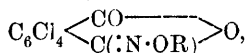
may be prepared: *methyl*, blades, m. p. 206°; *ethyl*, m. p. 160°; iso*propyl*, very thin, glistening plates or clusters of stout prisms, m. p. 146°; iso*amyl*, m. p. 244°; *allyl*, m. p. 186°; and *benzyl*, filaments only, m. p. 192°. The acetate (*ibid.*) and *benzoate*, pearly, diamond-shaped plates or stout prisms, m. p. 210°, are also obtained from the silver salt.

Tetrachlorophthalic anhydride phenylhydrazone,

$$C_6Cl_4 \diagdown{}^{CO\text{------}}_{C(:N\cdot NHPh)} \diagup O,$$
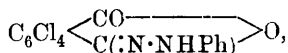
from the anhydride, phenylhydrazine, and glacial acetic acid, crystallises in yellow plates, which rapidly pass into orange needles, m. p. 287°. All m. p.'s are "corrected." [See also *Ind.*, April.]

J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. XIII. Tetra-iodophthaloxime and some of its Derivatives. DAVID S. PRATT and THOMAS B. DOWNEY (*J. Amer. Chem. Soc.*, 1918, **40**, 412—415).—Tetra-iodophthalic anhydride (this vol., i, 177) has been converted into *tetra-iodophthaloxime*,

$$C_6I_4 \diagdown{}^{CO\text{------}}_{C(:N\cdot OH)} \diagup O,$$
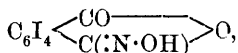
which exists in only one form, long, lemon-yellow needles of no definite m. p. From the red *silver* salt, the *methyl*, *ethyl*, n-*propyl*, iso*propyl*, n-*butyl*, iso*amyl*, n-*octyl*, *allyl*, and *benzyl* ethers, and the *acetate* and *benzoate*, have been obtained. These all crystallise in more or less pale yellow needles, and also decompose without melting. [See also *Ind.*, April.]   J. C. W.

The Structure of Truxillic Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 590—596).—From a consideration of their properties, their inter-conversion, and their preparation from cinnamic acids, the author has assigned spacial formulæ to the α-, β-, γ-, δ-, and ε-truxillic acids and to β-cocaic acid, on the assumption that these acids contain a tetramethylene ring.   W. G.

New Synthesis of Digallic Acid, and Migration of Acyl in the Partial Hydrolysis of Acylated Phenolcarboxylic Acids. EMIL FISCHER, MAX BERGMANN, and WERNER LIPSCHITZ (*Ber.*, 1918, **51**, 45—79).—Two syntheses have already been described which were expected to lead to *p*-digallic acid, but yielded

m-digallic acid instead (A., 1908, i, 893; 1911, i, 875; 1913, i, 479). A third method is now described. 3:5-Diacetylgallic acid is condensed with triacetylgalloyl chloride, giving penta-acetyl-*p*-digallic acid, and this is cautiously hydrolysed by cold, dilute ammonia solution. Again, the surprising discovery has been made that the product is *m*-digallic acid.

Similarly, if 3:5-diacetylgallic acid is benzoylated and the acetyl groups are removed by hydrolysis, the product is not para-, but *m*-benzoylgallic acid, and when 4-benzoyloxy-3-acetoxybenzoic acid is partly hydrolysed, the product is 3-benzoylprotocatechuic acid.

All these unexpected products are therefore due to the wandering of one acyl group into the position vacated on hydrolysis by another attached to a neighbouring carbon atom. Thus:

$$\begin{array}{ccc}
\text{CO}_2\text{H} & \text{CO}_2\text{H} & \text{CO}_2\text{H} \\
\text{OAc} \quad \text{OAc} & \text{OH} \quad \text{OBz} & \text{OH} \quad \text{O} \\
\text{OBz} & \text{OH} & \text{O--CPh·OH} \\
\text{(I.)} & \text{(II.)} & \text{(III.)}
\end{array}$$
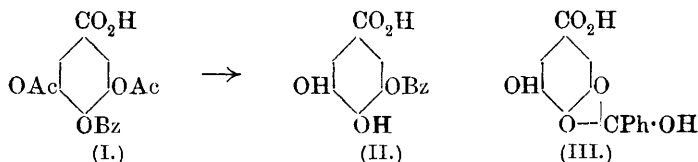
A transference of an acyl group has often been reported before, but only from carbon to oxygen or nitrogen and vice versa, or from nitrogen in a side-chain to nitrogen in the ring, numerous references to which are quoted, but this is the first record of such a migration from one phenolic group to another. The intermediate compound, (III), might perhaps be formed. ´

DERIVATIVES OF GALLIC ACID.—Triacetylgallic acid is conveniently obtained by adding granulated zinc chloride (50 grams) to a mixture of gallic acid (500) and acetic anhydride (2500). If too much zinc chloride is used, considerable quantities of *triacetylgallic* [3:4:5-*triacetoxybenzoic*] *anhydride*, m. p. 175—176° (corr.), are formed as well. Pyridine and acetic anhydride may also be used. The acid has m. p. 171—172° (corr.), crystallises well, and forms a sparingly soluble silver salt and dark blue *copper* salt. The *chloride* is obtained in well-developed prisms, m. p. 106—107° (corr.), by the action of phosphorus pentachloride. The acid is hydrolysed to 3:5-*diacetylgallic* [3:5-*diacetoxy-4-hydroxybenzoic*] *acid*, $C_{11}H_{10}O_7,H_2O$, stout spikelets, m. p. 174—175° (corr.), by dissolving it in the required quantity of concentrated potassium hydrogen carbonate solution, and slowly adding cold 2*N*-sodium hydroxide (1¼ mols.), the mixture being kept below 0° and well stirred, and hydrogen being passed through without interruption. Some gallic acid and a *monoacetylgallic* [*acetoxydihydroxybenzoic*] *acid*, m. p. 225° (decomp.), are also formed, and a good deal of the triacetate escapes hydrolysis. The diacetate is methylated by means of diazomethane, the product being *methyl* 3:5-*diacetoxy-4-methoxybenzoate*, elongated tablets or prisms, m. p. 68—69°, which may be hydrolysed by cold, dilute sodium hydroxide in a current of hydrogen to the known 3:5-dihydroxy-4-methoxybenzoic

acid (gallic acid 4-methyl ether) (A., 1912, i, 559). This proves the constitution of the diacetate.

*Penta-acetyl-*p*-digallic   acid*   [4-(3':4':5'-*triacetoxybenzoyloxy*)-3:5-*diacetoxybenzoic acid*] is prepared by the interaction of tri-acetylgalloyl chloride and 3:5-diacetylgallic acid in cold, aqueous acetone in the presence of just sufficient dilute sodium hydroxide or potassium hydrogen carbonate. It forms thin needles, m. p. 202—203° (corr.), yields a *methyl* ester, m. p. 192—193° (corr.), and a *chloride*, m. p. 164—167° (corr.), and is hydrolysed by shaking with 5N-ammonia (8—9 mols.) in the cold, and in the absence of air, to *m*-digallic acid. This yields the methyl pentamethyl-*m*-digallate of definite constitution, and may also be shown not to be a para-derivative by the fact that on acetylation it yields a different penta-acetate. Penta-acetyl-*m*-digallic acid crystallises in stout prisms, m. p. 204—205° (corr.) (given in A., 1913, i, 479, as 193—194°), and forms a *methyl* ester, m. p. 167—168° (corr.). Similarly, the above methyl penta-acetyl-*p*-digallate yields *methyl* m-*digallate*, 1H_2O, m. p. 175°, when cautiously hydrolysed by ammonia. This gives a bluish-black coloration with ferric chloride, and yields pre-cipitates with pyridine, quinoline, brucine, and quinine salts; it may also be obtained by the action of dilute ammonia on methyl penta-acetyl-*m*-digallate, or converted into this by acetylation.

3:5-Diacetylgallic acid is benzoylated under the same conditions as observed in the above acylation. A small amount of a *benzoyl-oxyacetoxybenzoic acid*, $OH \cdot C_6H_2AcBz \cdot CO_2H$, m. p. 174—176° (corr.), is formed, but the main product is the desired 4-*benzoyl-3:5-diacetylgallic* [4-*benzoyloxy-3:5-diacetoxybenzoic*] *acid* (I). This crystallises in well-developed tablets or prisms, m. p. 183—184° (corr.), forms a *methyl* ester, m. p. 138—139° (corr.), and may be hydrolysed by means of 5N-hydrochloric acid in acetic acid at 85—90°, or by ammonia at 0°, or by warming with sodium acetate, the first being the best method, to 3-*benzoylgallic* [3-*benzoyloxy-4:5-dihydroxybenzoic*] *acid* (II), which has m. p. 240—242° (corr.), and gives a bluish-green colour with ferric chloride and a deep red with potassium cyanide. When treated with diazo-methane, this yields *methyl 3-benzoyloxy-4:5-dimethoxybenzoate*, in stout tablets, m. p. 91—92°, which may be hydrolysed to the known 3-hydroxy-4:5-dimethoxybenzoic acid (3:4-dimethylgallic acid), m. p. 197—198° (corr.). Similarly, the above methyl 4-benzoyl-3:5-diacetylgallate may be converted into *methyl 3-benzoyloxy-4:5-dihydroxybenzoate*, stout plates or prisms, m. p. 173—175° (corr.), and this into the above ester, m. p. 91—92°, or into *methyl 3-benzoyloxy-4:5-diacetoxybenzoate*, elongated, flat, hexagonal tablets, m. p. 110—111°. 3-Benzoylgallic acid may also be reacetylated by means of pyridine and acetic anhydride, yield-ing the isomeric 3-*benzoyloxy-4:5-diacetoxybenzoic acid*, which crystallises in thin, curved needles, m. p. 177—178° (corr.), and may be esterified to the same ester as above (m. p. 110—111°), or hydrolysed again to 3-benzoylgallic acid.

4:5-Carbonylogallic acid (A., 1913, i, 479) yields 3-*benzoyloxy-*
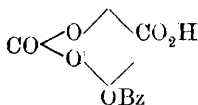
4 : 5-*carbonyldioxybenzoic acid* (annexed formula) when shaken with benzoyl chloride and pyridine. This crystallises in thin, hexagonal tablets, m. p. 207—210° (corr.), and is hydrolysed to 3-benzoylgallic acid by boiling with acetone and water.

$$CO {<}^{O}_{O}{>} \quad \overset{}{\underset{OBz}{\diagup}} CO_2H$$

DERIVATIVES OF PROTOCATECHUIC ACID.—Protocatechuic acid is most conveniently acetylated by the method used in the case of gallic acid. The diacetylprotocatechuic acid [3 : 4-diacetoxybenzoic acid], m. p. 157—158° (corr.), is partly hydrolysed, also by the method applied to triacetylgallic acid, the product being 3-acetyl-protocatechuic acid, m. p. 202—203° (corr.), apparently identical with an acid described by Ciamician and Silber in 1892. The constitution is proved by the fact that it is converted by diazomethane into methyl 3-acetoxy-4-methoxybenzoate, m. p. 87—88°, which may be hydrolysed to 3-hydroxy-4-methoxybenzoic acid (*iso*vanillic acid). 4-*Benzoyloxy*-3-*acetoxybenzoic acid* is obtained by benzoylation, in whet-stone forms, m. p. 154—155° (corr.). This yields a *methyl* ester, m. p. 102—103° (corr.), and may be hydrolysed by means of 5N-hydrochloric acid mixed with acetic acid, at 100°, to 3-*benzoyloxy*-4-*hydroxybenzoic acid*. This crystallises in microscopic needles, m. p. 225—227° (corr.), and forms *methyl 3-benzoyloxy-4-methoxybenzoate*, m. p. 101—102°, when treated with diazomethane, this being also obtained by benzoylating methyl *iso*vanillate. Similarly, the above methyl 4-benzoyloxy-3-acetoxy-benzoate may be hydrolysed by ammonia to *methyl 3-benzoyloxy-4-hydroxybenzoate*, hexagonal tablets, m. p. 153·5—155° (corr.), which yields *methyl 3-benzoyloxy-4-acetoxybenzoate*, in long, thin prisms, m. p. 54—55°, on acetylation. J. C. W.

Phthalic Acid Derivatives. Constitution and Colour. VIII. Tetraiodofluorescein and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 236—245. Compare this vol., i, 168, 169, 170).—*Tetraiodofluorescein*, $C_{20}H_8O_5I_4$, obtainable from tetraiodophthalic anhydride and resorcinol by heating with zinc chloride, exists at the ordinary temperature as an unstable mixture of the benzenoid and quinonoid modifications. Its solutions in dilute aqueous alkali possess a yellowish-red colour and a vivid green fluorescence, and on acidification deposit a golden-yellow *hydrate*; this, when freshly precipitated, appears to contain loosely combined water, but after drying at the ordinary temperature in the air for a few days retains only approximately one molecule of water, for the removal of which a temperature of 120° is necessary; the first dehydration process does not affect the colour, but the passage into the anhydrous compound is accompanied by a change to reddish-brown, due to a partial conversion of the benzenoid into the quinonoid form; the hydrate is believed to be of the benzenoid structure. The application of a drop of acetone, alcohol, or ethyl acetate to the reddish-brown, anhydrous compound causes an immediate change of colour to a clear canary-yellow, due to rearrangement into the more stable benzenoid

modification. This behaviour is in marked contrast to that of fluorescein, which has never been isolated in the benzenoid condition. Treatment of the freshly precipitated tetraiodofluorescein with a little methyl or ethyl alcohol immediately converts it into the very pale yellow carbinol–carboxylic acid, the structural change being represented by the difference between formulæ I and II.

$$CO<\!\!\begin{array}{c}C_6H_3(OH)\\C_6H_3(OH)\end{array}\!\!>C<\!\!\begin{array}{c}-O-\\C_6I_4\end{array}\!\!>C(OH)_2$$
(I.)

$$CO<\!\!\begin{array}{c}C_6H_3(OH)\\C_6H_3(OH)\end{array}\!\!>C(OH)\cdot C_6I_4\cdot CO_2H$$
(II.)
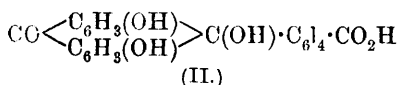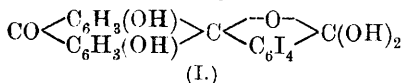
The anhydrous tetraiodofluorescein was also converted into the reddish-orange *potassium* salt, deep red *diammonium* salt, red *silver* salt, amorphous, bright red *methyl ether*, $C_{21}H_{10}O_5I_4$, decomp. near 251°, *diacetate*, $C_{24}H_{12}O_7I_4$, yellow crystals, and *dibenzoate*, $C_{34}H_{16}O_7I_4$, pale yellow crystals, m. p. 288° (corr.).   D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. IX. Tetraiodoeosin and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 245—249. Compare preceding abstract).—Tetraiodofluorescein is readily brominated in acetic acid solution with formation of *tetraiodoeosin*, $C_{20}H_4O_5Br_4I_4$, canary-yellow crystals, which show no tendency to pass into a highly coloured quinonoid form, and are therefore presumably of benzenoid constitution. It dissolves in aqueous alkalis, yielding deep red solutions with faint green fluorescence, from which dilute hydrochloric acid precipitates a pink, amorphous *hydrate*, $3C_{20}H_4O_5Br_4I_4,H_2O$. Ammonia converts the solid tetraiodoeosin into a red *diammonium* salt,
$$C_{20}H_4O_5Br_4I_4,2NH_3,$$
whilst the *silver* salt, $C_{20}H_3O_5Br_4I_4Ag$, obtained by precipitation, is reddish-purple. *Tetraiodoeosin methyl ether*, $C_{21}H_6O_5Br_4I_4$, obtained by the action of methyl sulphate in the presence of alkali, is a red, amorphous powder, whilst the *diacetate*, $C_{24}H_8O_7Br_4I_4$, and *dibenzoate*, $C_{34}H_{12}O_7Br_4I_4$, form pale yellow crystals, m. p. 270—280° and near 261° respectively, with liberation of iodine in both cases.   D. F. T.
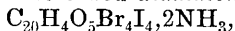
Phthalic Acid Derivatives. Constitution and Colour. X. Tetraiodoerythrosin (Octaiodofluorescein) and some of its Derivatives. DAVID S. PRATT and ARTHUR B. COLEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 249—254. Compare preceding abstracts).—*Octaiodofluorescein*, $C_{20}H_4O_5I_8$, is most conveniently obtained by heating tetraiodofluorescein with iodine and iodic acid in alcoholic solution for twelve hours. When free from combined solvent, the compound forms clear, yellow crystals, but at 140° it becomes dark red, probably due to a transformation from the benzenoid to the quinonoid constitution. With acetone, it forms a yellow *additive* compound, $C_{20}H_4O_5I_8,C_3H_6O$, which is decomposed into its con-

stituents at 120°. Gaseous ammonia converts the solid octaiodo-fluorescein into a red *tetrammonium* salt, $C_{20}H_4O_5I_8,4NH_3$, whilst the *silver* salt, $C_{20}H_3O_5I_8Ag$, obtained by precipitation, is violet. The *methyl ether*, $C_{21}H_6O_5I_8$, prepared by the action of methyl sulphate, is an unstable, dark red, non-crystalline substance, whilst the *diacetate*, $C_{24}H_6O_7I_8$, and the *dibenzoate*, $C_{34}H_{12}O_7I_8$, form yellow crystals, decomp. above 200° and m. p. near 300° respectively. D. F. T.

Phthalic Acid Derivatives. Constitution and Colour. XI. Phenoltetraiodophthalein and some of its Derivatives.

DAVID S. PRATT and ASHER F. SHUPP (*J. Amer: Chem. Soc.*, 1918, **40**, 254—264. Compare preceding abstracts).—Tetraiodophthalic anhydride, yellow needles, m. p. 320—325° (corr.), obtained by heating phthalic anhydride and iodine with fuming sulphuric acid, when heated with an excess of phenol with the gradual addition of sulphuric acid, undergoes condensation with formation of phenoltetraiodophthalein, yellow crystals, m. p. 239—245° (compare Rupp, A., 1911, i, 301), which give a deep red solution in aqueous alkali. The phthalein is probably of benzenoid constitution, the yellow colour being attributed to the influence of the iodine atoms in bringing the absorption into the visible spectrum. It yields a *diacetate*, $C_{24}H_{14}O_6I_4$, pale yellow crystals, m. p. 230° (corr.), a *dibenzoate*, $C_{34}H_{18}O_6I_4$, pale yellow needles, m. p. 236° (corr.), a *dimethyl ether*, $C_{22}H_{14}O_4I_4$, yellow crystals, m. p. 221° (corr.), a *dinitro*-derivative, $C_{20}H_8O_8N_2I_4$, yellow needles, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{12}O_{10}N_2I_4$, deep yellow crystals, m. p. 281°, corr.), a *tetranitro*-derivative, $C_{20}H_6O_{12}N_4I_4$, yellow crystals, decomp. near 311° (corr.), and a *tetrabromo*-derivative,

$$C_{20}H_6O_4Br_4I_4,$$

yellow crystals, m. p. 311—312° (corr.) (*diacetate*, $C_{24}H_{10}O_6Br_4I_4$, yellow crystals, m. p. 285°, corr.; *dibenzoate*, $C_{34}H_{14}O_6Br_4I_4$, yellow crystals, m. p. 213—215°, corr.; *dimethyl ether*, $C_{22}H_{10}O_4Br_4I_4$, yellow crystals, m. p. 255°, corr.). By treatment in cold aqueous alkaline solution with a solution of iodine in potassium iodide it is possible to convert phenoltetraiodophthalein into *tetraiodophenoltetraiodophthalein*, $C_{20}H_6O_4I_8$, deep yellow crystals, m. p. 285° (corr., with decomp.); this forms a *diacetate*, $C_{24}H_{10}O_6I_8$, pale yellow crystals, m. p. 288° (corr.), a *dibenzoate*, $C_{34}H_{14}O_6I_8$, pale yellow crystals, m. p. 202—203° (corr.), and a *dimethyl ether*, $C_{22}H_{10}O_4I_8$, pale yellow crystals, decomp. at 295—297° (corr.). D. F. T.

Laurent's Benzimide (Benzylidenebenzaldehydecyanhydrin-acetal).

MARIA SAVELSBERG (*J. pr. Chem.*, 1917, [ii], **96**, 186. Compare A., 1916, i, 728).—An acknowledgment of the priority of Stolle (A., 1902, i, 468) in the observation of the formation of an acetal compound by the condensation of mandelonitrile and benzaldehyde. D. F. T.

Derivatives of Veratrole. ADOLF KAUFMANN and HERMANN MÜLLER (*Ber.*, 1918, **51**, 123—130).—I. DERIVATIVES OF *o*-VERATR-ALDEHYDE.—2 : 3-*Dimethoxybenzyl alcohol* (*o-veratryl alcohol*) is obtained by reducing the aldehyde with hydrogen and platinum-black ; it crystallises in very long, massive, transparent, rectangular columns, m. p. 50°, and is converted into the *chloride*, b. p. 128·5—129°/11 mm., by means of thionyl chloride. The chloride rather easily loses hydrogen chloride on distillation under higher pressures, suffering condensation to an anthracene derivative. It also combines with methylnorhydrastinine, but the normal quatern-ary chloride (I) cannot be isolated, neither can the corresponding base. The solution, however, gives precipitates of a *perchlorate* and a *picrate*, m.·p. 223—225°, whilst a *benzoyl* derivative, m. p. 146°, probably of the formula II, may be obtained by the Schotten-Baumann method.

(I.)

(II.)
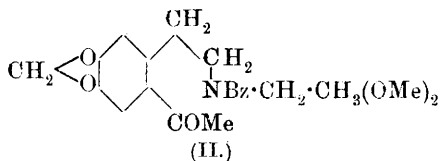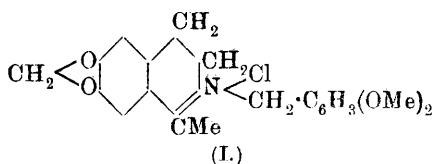
Veratraldehyde and homopiperonylamine condense to form *o-veratrylidenehomopiperonylamine*, white needles, m. p. 59—60°, which may be hydrogenated in the presence of palladium-black to *o-veratrylhomopiperonylamine* (2 : 3-*dimethoxybenzyl-β-3 : 4-methyl-enedioxyphenylethylamine*),

$$CH_2{:}O_2{:}C_6H_3{\cdot}CH_2{\cdot}CH_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_3(OMe)_2,$$

a viscous oil, which forms a *hydrochloride*, $1H_2O$.

II. *p*-DERIVATIVES OF VERATROLE.—*p*-*Homoveratronitrile* (3 : 4-*dimethoxyphenylacetonitrile*) is obtained in long, colourless needles, m. p. 64—65°, b. p. 171—178°/10 mm., by heating the corresponding aldoxime with acetic anhydride.

ω - Bromoacetoveratrone [3 : 4 - dimethoxyphenyl bromomethyl ketone] (Mannich and Hahn, A., 1911, i, 649) reacts with potassium acetate in boiling alcohol to form the *acetate* (glistening tablets, m. p. 91—92°) of *p-veratroylcarbinol* (3 : 4-*dimethoxybenzoylmethyl alcohol*), which separates in transparent crystals, m. p. 86—87°.

III. DERIVATIVES OF DIMETHOXYBENZOIN.—Veratrole condenses with phenylacetyl chloride under the influence of aluminium chloride to form 3 : 4-*dimethoxydeoxybenzoin* (3 : 4-*dimethoxyphenyl benzyl ketone*) in white needles, m. p. 88°. A *bromide*, pale yellow crystals, m. p. 116—117°, is produced when the required quantity of bromine is carried by a stream of carbon dioxide into a solution of this in carbon disulphide, and *p*-toluenesulphomethylamide reacts

with this bromide to form 3 : 4-*dimethoxyphenyl* α-p-*toluenesulphonylmethylaminobenzyl ketone*,

$$C_6H_4Me \cdot SO_2 \cdot NMe \cdot CHPh \cdot CO \cdot C_6H_3(OMe)_2,$$

in white crystals, m. p. 180°.   J. C. W.

The Beckmann Rearrangement. VIII. Mitsuru Kuhara, Naomichi Agatsuma, and Kiukichi Araki (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1917, III, (1), *Reprint*, 16 pp.).—Kuhara and his colleagues have already shown that the esters of oximes derived from strong acids, for example, benzenesulphonates, spontaneously suffer the Beckmann rearrangement, whereas the addition of an acid like hydrochloric acid is necessary in order to bring about the change in esters of weak acids, like acetates. It is now suggested that the function of hydrochloric acid is to expel the weak acid, giving the oxime chloride which is immediately rearranged. Thus, in the case of diphenylketoxime acetate, the reaction is represented as follows:
$CPh_2 : N \cdot OAc + HCl \longrightarrow MeCO_2H + CPh_2 : NCl \longrightarrow CPhCl : NPh$. It is impossible to isolate these chlorine derivatives, as the reaction proceeds further to the production of benzanilide, but if the acetate is heated with benzenesulphonic acid at 95—97°, an analogous product, phenylbenziminobenzenesulphonate (A., 1915, i, 144) may be recovered, thus:

$$CPh_2 : N \cdot OAc + OH \cdot SO_2Ph \longrightarrow MeCO_2H + CPh_2 : N \cdot O \cdot SO_2Ph \longrightarrow$$
$$NPh : CPh \cdot O \cdot SO_2Ph.$$
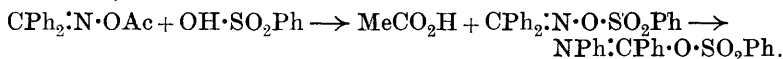
The same idea may be applied in explaining the rearrangement of the hydrochlorides of oximes under the influence of dehydrating agents. The hydrochloride of diphenylketoxime changes instantly into benzanilide when heated at 128°, quickly when heated with zinc chloride or chloral at 90°, and within a day or two at 25° when mixed with chloral. The change is formulated thus:

$$CPh_2 : N \cdot OH, HCl - H_2O \longrightarrow CPh_2 : NCl \longrightarrow$$
$$CPhCl : NPh \xrightarrow{H_2O} NHPh \cdot COPh.$$
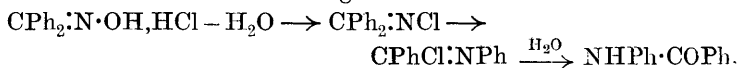
In the case of the methyl ether hydrochloride, $CPh_2 : N \cdot OMe, HCl$, methyl chloride is lost at above 45°, and no trace of the oxime suffers rearrangement, owing to the absence of the necessary :NCl group. The same interpretation is given to the rearrangement of diphenylketoxime by phosphorus pentachloride. If this agent is gradually added to an ethereal solution of the oxime, it first disappears, then the white hydrochloride of the oxime separates, and finally, when an equivalent has been added, a yellow chlorine compound is formed, which changes into benzanilide on adding water, thus: $2CPh_2 : N \cdot OH + PCl_5 \longrightarrow CPh_2 : NCl + CPh_2 : N \cdot OH, HCl \xrightarrow[-H_2O]{+PCl_5}$ $CPh_2 : NCl$, and this $\longrightarrow NPh : CPhCl$.

What at first sight is a weak point in Kuhara's argument is the fact that chloroiminodiphenylmethane, $CPh_2 : NCl$, when prepared by the action of hypochlorous acid on iminodiphenylmethane, resists the transforming influence of a large variety of agents (compare Stieglitz and Stagner, A., 1917, i, 22). If, however, the

chloro-imine is fused with potassium hydroxide, the rearrangement takes place with almost explosive violence, aniline and benzophenone being formed. The unsubstituted imine, and also diphenylketoxime and its acetate, do not yield aniline under the same treatment. The authors' explanation is that the chlorine atom in the stable chloro-imine is positively charged, and requires to be negatively charged before spontaneous rearrangement can take place, which alteration is brought about by the molten alkali, thus:
$CPh_2{:}NCl^+$ $\xrightarrow{KOH}$ $CPh_2{:}NCl^-$ $\longrightarrow$ $NPh{:}CPhCl^-$.

Evidence is also given to show that the ease with which the oxime esters undergo rearrangement is mutually dependent on the nature of the acid radicle and the hydrocarbon residues. Thus, the following benzenesulphonates suffer rearrangement at different temperatures: $CPh_2{:}NX$, 62°; $(CH_2Ph)_2C{:}NX$, 74°; $CMe_2{:}NX$, 130°; $CMePh{:}NX$, 81—82°; $\begin{smallmatrix}OEt \cdot CPh\\ \parallel \\ NX\end{smallmatrix}$, 95—96°; whilst the following esters of diphenylketoxime vary in stability, according to the strength of the acid: $CPh_2{:}N{\cdot}O{\cdot}SO_2Ph$, 62°;
$$CPh_2{:}N{\cdot}O{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2(m),\ 24°;$$
$CPh_2{:}N{\cdot}O{\cdot}CO{\cdot}CH_2Cl$, above 195°; and $CPh_2{:}N{\cdot}OAc$, which does not change on heating. It appears, therefore, that the exchange of groups in the rearrangement is simultaneous.

Dibenzylketoxime benzenesulphonate (above) forms colourless crystals, m. p. 64°; the *acetate* has m. p. 33—34°, and the *benzoate*, m. p. 60·5°. *Diphenylketoxime* m-*nitrobenzenesulphonate* (above) has m. p. 24°, and the *chloroacetate* (above) also has m. p. 24°.

<div align="right">J. C. W.</div>

Preparation of Dihydroxyanthraquinones and their Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 298345, 1916; from *Chem. Zentr.*, 1917, ii, 256).—It is possible to effect the condensation of phenols, naphthols, hydroxyanthracenes, and similar substances with phthalic anhydride under the influence of aluminium chloride with production of anthraquinone derivatives in one operation if the reaction mixture is heated at approximately 180—250°; it is advantageous to use an excess of phthalic anhydride to act as solvent. In this way catechol gives hystazarin free from alizarin, in considerably greater yield than when sulphuric acid is used; α-naphthol yields pure hydroxynaphthacene-quinone, whilst β-naphthol gives hydroxynaphthanthraquinone, yellow needles. Hydroxyanthracenes and hydroxyanthraquinones reduced at the ketonic groups, for example, leucoquinizarin and deoxyalizarin, can also be condensed to hydroxyanthraquinone compounds. Pyrogallol yields anthragallol, yellow needles. The patent also refers to the formation of condensation products of phthalic anhydride with 1- and 2-hydroxyanthraquinones, 1:4:9:10-tetra-hydroxyanthracene, deoxyalizarin, and 2:7-dihydroxynaphthalene, the product in the last case crystallising in yellow needles. 3:6-Di-chlorophthalic acid and α-naphthol undergo condensation with

formation of a compound crystallising in brown needles and soluble in sulphuric acid to a violet solution. D. F. T.

1 : 4 : 6-Trihydroxyanthraquinone. M. L. CROSSLEY (*J. Amer. Chem. Soc.*, 1918, **40**, 404—406).—4-Aminophthalic anhydride (Bogert and others, A., 1902, i, 98; 1906, i, 510) condenses with quinol in concentrated sulphuric acid at 170—190° to form some 6-amino-1 : 4-dihydroxyanthraquinone (?), but chiefly 1 : 4 : 6-*trihydroxyanthraquinone*, which is a reddish-brown powder, not molten at 300°, and gives bluish-violet solutions in alkali hydroxides. It has no particular value as a mordant dye. [See also *Ind.*, April.] J. C. W.

Hydrogenation of Olefinic Terpene Alcohols, Aldehydes, and Acids. CARL PAAL (D.R.-P., 298193, 1913; from *Chem. Zentr.*, 1917, ii, 145—146).—Under suitable conditions it is possible to reduce alcohols, aldehydes, and acids of the terpene group by hydrogen and palladium or platinum, the ethylenic linking becoming hydrogenated, and two ethylene linkings, if present, being capable of successive hydrogenation, without affecting the alcoholic, aldehydic, or acidic group. It is thus possible to reduce citral successively into citronellal and dihydrocitronellal; geraniol successively into citronellol and dihydrocitronellol; linalool successively into its dihydro- and tetrahydro-derivatives, and geranic acid successively into dihydrogeranic acid (*r*-citronellic acid) and tetrahydrogeranic acid. The palladium or platinum catalyst may be used in the colloidal condition, but for the present purpose the palladous or platinous hydroxide, or the metals themselves deposited on powders free from any anti-catalytic effect, are especially suited. A deposit of palladium or platinum may be formed on magnesium, nickel, or cobalt by immersing these metals in a solution of a palladium or platinum salt, or by treating precipitated magnesium oxide or carbonate or calcium carbonate with a solution of bivalent palladium or platinum it is possible to coat these powders with palladous or platinous hydroxide. Another method is to soak an indifferent powder, such as barium sulphate, infusorial earth, carbon, and cellulose powder with a solution of palladous or platinous salt, and then to precipitate the hydroxide of the rare metal on the powder by treating with sodium carbonate solution. With palladium or palladous hydroxide a convenient proportion of catalyst to carrier is 0·5—1%, whilst with platinum and its hydroxide it is 1—2%.

D. F. T.

The Colouring Matters of Camwood, Barwood, and Sanderswood. PAULINE O'NEILL and ARTHUR GEORGE PERKIN (T., 1918, **113**, 125—140).—The well-known red dye-woods, sanderswood, barwood, caliaturwood, and camwood, are very similar in tinctorial properties. In fact, the first three might well contain the same pigment, but camwood dyes mordanted wool somewhat bluer tones and is more readily extracted by water. A chemical comparison of the camwood pigment with the santalin of

sanderswood, recently investigated by Cain and Simonsen (T., 1912, **101**, 1061), appeared to be desirable, and a preliminary account of a research in this connexion is now given.

The chief, more insoluble colouring matter of camwood is found to be an isomeride of santalin, designated iso*santalin*. It decomposes at a higher temperature than santalin (250—280°, as against 250—260°) and dyes bluer shades. For many reasons, both pigments are best expressed as $C_{22}H_{18}O_6(OMe)_2$, instead of $C_{14}H_{11}O_4(OMe)$. Both woods contain more soluble dyes, which are again isomeric. For these, the names *deoxysantalin* and *deoxy*isosantalin, and the formula $C_{22}H_{16\,or\,18}O_5(OMe)_2$, are proposed. Not much can be said as to the relation between the santalins and the deoxysantalins, except that the results of acetylation do not indicate that the former possess one more hydroxyl group than the latter. The deoxysantalins are the better pigments.

The first pigment to be isolated from sanderswood was that obtained by Meier (1848), which is apparently deoxysantalin rather than santalin, although the present authors were not so successful in obtaining a crystalline specimen. In 1870, Weidel also obtained from sanderswood, santal, which is now written as $C_{15}H_9O_5·OMe$, and a bright red substance, which is now designated *santalone*, and is possibly deoxysantalin monomethyl ether, $C_{22}H_{15}O_4(OMe)_3$. These are difficult to obtain from sanderswood, but they have now been extracted from barwood, which contains santalin as well. Santal crystallises in large, colourless leaflets, m. p. 222—223°, and yields *santol*, flat needles, m. p. 270—273°, on demethylation by Zeisel's method. Santalone forms glistening, red leaflets, m. p. 300°.

The colouring matter in the flower of St. John's wort is quercetin, and not gossypetin, as Keegan suggested (A., 1915, i, 758).

For experimental details, see the original.   J. C. W.

The Mechanism of the Formation of certain Isomerides of Cinchonine and of their Hydrohaloid Derivatives. E. LÉGER (*Compt. rend.*, 1918, **166**, 255—258. Compare this vol., i, 121).—Admitting for cinchonine the constitution (formula I) and for cinchonigine and cinchoniline the constitu-

$$CH_2:CH·C_{16}H_{17}N_2:CH(OH)^-$$

$$CHMe·[C_{16}H_{17}N_2:CH]$$
$$O———————O$$

(I.)   (II.)
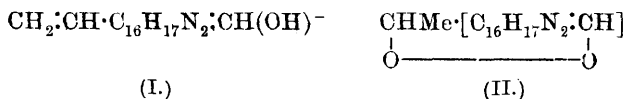
tion (formula II), and for *apo*cinchonine, $CHMe:C_{16}H_{16}N_2:CH·OH$, this latter being formed from cinchonine by the addition and subsequent removal of the elements of water, it is easy to see that the fixation of hydrogen bromide will in all four cases give the same hydrobromocinchonine. But the four compounds are optically active, and it must be supposed that the fixation of hydrogen bromide is preceded, in certain cases, by stereoisomeric changes. It is probable that cinchonine and cinchoniline have the same

steric arrangement, their isomerism being due to differences of structure. In the cases of cinchonigine and *apo*cinchonine, there is a formation of their normal hydrobromo-derivatives, and at the same time a partial transformation into cinchoniline, which then yields hydrobromocinchonine. **W. G.**

A Synthesis of 2 : 6-Dimethylcinchomeronic Acid and 2 : 6-Lutidine. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1917, **50**, 1568—1584).—Some years ago, Mumm and Bergell found that the ammonium salt of acetylpyruvic acid gradually loses water to form 3-acetyl-4-methylpyridine-2 : 6-dicarboxylic acid, and this was explained on the assumption that the ammonium salt changes partly into an acid of the formula $CH_3\cdot CO\cdot CH:C(NH_2)\cdot CO_2H$, which condenses with a further portion of the salt (A., 1912, i, 936). If this view is correct, it should be possible to effect such a pyridine synthesis, using other compounds of the type of acetylpyruvic acid on the one hand, and the above unsaturated amino-acid on the other. It is now shown that ethyl acetylpyruvate and ethyl β-aminocrotonate react vigorously at 0° to form ethyl 2 : 6-dimethylcinchomeronic acid, the constitution of which is revealed by the facts that the corresponding potassium salt yields 2 : 6-lutidine on distillation with lime, and that the free acid gives an anhydride.

Ethyl acetylpyruvate, which is obtained by Claisen's method from ethyl oxalate and acetone, reacts equally well with ethyl β-aminocrotonate at 0°, whether undiluted or mixed with alcohol or ether, giving a 90% yield of *ethyl 2 : 6-dimethylpyridine-3 : 4-dicarboxylate*, which is a pale yellow, viscous oil, b. p. 163°/ 13 mm., m. p. 16°, and gives a *hydrochloride*, quadratic tablets, m. p. 121°, a *picrate*, clusters of stout needles, m. p. 101°, and a *platinichloride*, yellow needles. If burnt in the ordinary way, the ester apparently forms a nitrogenous compound which escapes combustion, so nitrogen was determined by Kjeldahl's method and carbon and hydrogen by Dennstedt's process. If the mixture is not cooled, the water liberated during the condensation may cause two other reactions with the parent substances, thus:

$$NH_2\cdot CMe:CH\cdot CO_2Et + H_2O = CH_2Ac\cdot CO_2Et + NH_3$$

and $CH_2Ac\cdot CO\cdot CO_2Et + NH_3 = CH_2Ac\cdot C(:NH)\cdot CO_2Et + H_2O$. That is, ethyl acetoacetate and *ethyl α-iminolaevulate* ("α-imide of ethyl acetylpyruvate" in the earlier paper) may be formed. The latter crystallises in thin prisms, m. p. 39°, b. p. 115°/13 mm.

The free 2 : 6-*dimethylpyridine-3 : 4-dicarboxylic acid* (2 : 6-*dimethylcinchomeronic acid*) crystallises by spontaneous evaporation of aqueous solutions in short, rhombic prisms, m. p. 275° (sealed capillary; decomp.). It is almost insoluble in most solvents. The *potassium* salt forms silky needles, and gives a 91% yield of 2 : 6-dimethylpyridine (2 : 6-lutidine), b. p. 142°, when distilled with calcium hydroxide, this being at present the most convenient method for making the pure lutidine. The acid also yields an *anhydride*, needles, m. p. 101°, when heated at 220°/vac., or with acetic

anhydride. It may be that Collie and Wilsmore were correct in a tentative suggestion that they had obtained the same acid by the oxidation of 8-hydroxy-1 : 3 : 6-trimethyl*iso*quinoline (T., 1896, **69**, 295).

If the diethyl ester is left with one equivalent of alcoholic potassium hydroxide, it is partly hydrolysed to the 3-*ethyl hydrogen ester* (annexed formula), small needles, m. p. 161°, whilst the anhydride dissolves in alcohol to form the 4-*ethyl hydrogen ester*, short, flat prisms, m. p. 151°.

On heating the ammonium salt of the acid at 230°, 2 : 6-*dimethylcinchomeronimide* sublimes in very long needles, m. p. 230°.

The diethyl ester reacts with alcoholic ammonia at 120° to form the *diamide*, slender needles, m. p. 220° (heating very rapidly; vigorous decomp.). The 3-*amic acid* (annexed formula), crystallising with $2H_2O$ in rhombic leaflets, is formed by dissolving the imide in $4N$-sodium hydroxide, whilst the 4-*amic acid*, $2H_2O$, long needles, m. p. 115°, is obtained by saturating a benzene solution of the acid anhydride with ammonia.   J. C. W.

Synthesis of some Pyridine-polycarboxylic Acids. OTTO MUMM and HUGO HÜNEKE (*Ber.*, 1918, **51**, 150—164).—The synthesis of 2 : 6-dimethylcinchomeronic acid (preceding abstract) opens up a convenient way to prepare tri- and tetra-carboxylic acids of pyridine.

Oxidation of the acid with alkaline permanganate sufficient for one methyl group gives rise to a 67% yield of two methylpyridine-tricarboxylic acids. The chief product is 2-*methylberberonic acid* (2-*methylpyridine*-3 : 4 : 6-*tricarboxylic acid*), which crystallises from water in stout, short, rhombic prisms, with $3H_2O$, decomp. 226° (anhydrous), and the lesser product is 6-*methylpyridine-2 : 3 : 4-tricarboxylic acid*, which forms long, thin prisms, or sometimes hexagonal tablets, and carbonises without obvious evolution of gas at 230—280°. The two acids differ in a remarkable way in their copper salts; the former gives a precipitate with cupric acetate in hot solutions, which dissolves on cooling, but the latter gives a precipitate in the cold, which dissolves on heating.

2-Methylberberonic acid loses carbon dioxide on heating with glacial acetic acid for some days, yielding 2-*methylpyridine*-3 : 4-*dicarboxylic acid*, in very long, thin prisms, m. p. 250—255°, which gives an *anhydride*, m. p. 92°, when boiled with acetic anhydride, this being also formed when the tricarboxylic acid is heated at 230° in a vacuum. The new dicarboxylic acid may be oxidised by alkaline permanganate to pyridine-2 : 3 : 4-tricarboxylic acid, which crystallises in thin, rectangular leaflets, $1\cdot 5H_2O$, m. p. 249°, and is identical with the acid obtained by the oxidation of cinchonine (Camps, A., 1902, i, 824).

Both methyl groups in the original acid may be oxidised if twice as much permanganate is used. The product is pyridine-2:3:4:6-tetracarboxylic acid, which crystallises from water in narrow tablets, $3H_2O$, m. p. 235°, and is identical with the acid prepared by Fischer and Täuber from flavenol (A., 1885, 400). When this is boiled with glacial acetic acid, it loses carbon dioxide and gives a tricarboxylic acid which is not identical with any pyridinetricarboxylic acid of definite constitution, such as the above 2:3:4-acid, and can therefore only be pyridine-3:4:6-tri-carboxylic acid. It is, however, crystallographically and chem-ically identical with berberonic acid obtained from berberine, and this synthesis confirms the structure already assigned to this acid. The acid crystallises with $2H_2O$, which it does not lose on exposure to the air, and has m. p. 243° (decomp.). J. C. W.

The Relative Stability of Cyclic Bases. V. J. von Braun (*Ber.*, 1918, **51**, 96—100. Compare A., 1909, i, 604; 1911, i, 563; 1917, i, 168, 169).—Two very different methods have been worked out for effecting the rupture of cyclic systems containing nitrogen, namely, the Hofmann reaction and treatment with cyanogen bromide, but it has recently been shown that the gradations of stability exhibited by many of these bases are the same whichever test is applied. One exception seems to be dihydroindole, which proves to be one of the most stable systems in the Hofmann degradation, but one of the weakest towards cyanogen bromide.

1-Methyl-2:3-dihydroindole reacts with cyanogen bromide in the cold according to the scheme: $C_6H_4{<}^{CH_2}_{NMe}{>}CH_2 + BrCN \longrightarrow$
(1)
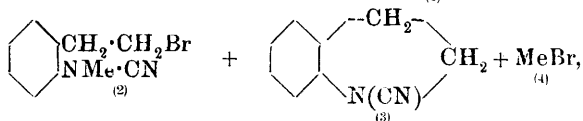
quaternary salts of (1) with (2) and (4) being formed as well, the yields being about 27% of (3) and 70% of (2), of which only 40% escapes the secondary reaction resulting in the quaternary salt. The quaternary salts are removed by ether as an insoluble, red oil, from which a small quantity of the *methobromide* of 1-methyl-dihydroindole, m. p. 195—197° (decomp.), may be recovered. The other bromide cannot be purified. The base (2) is charac terised by warming the soluble products with dimethylamine dis solved in benzene, when it is converted into *cyanomethyl-o-β-dimethylaminoethylaniline*, $NMe_2 \cdot C_2H_4 \cdot C_6H_4 \cdot NMe \cdot CN$. This may be extracted from the benzene by dilute sulphuric acid; it is a pale yellow oil, b. p. 175—178°/16 mm., which exhibits pale green fluorescence in alcoholic solution, forms a *picrate*, m. p. 142°, a *platinichloride*, m. p. 144°, a *methiodide*, m. p. 170°, and may be hydrolysed by means of concentrated hydrochloric acid at 150° to *methyl-o-β-dimethylaminoethylaniline*,

$$NMe_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_4 \cdot NHMe.$$
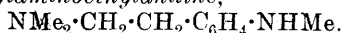
This base is a pale yellow oil, b. p. 138—139°/15 mm., which forms a *picrate*, m. p. 165—166°, a *platinichloride*, $2H_2O$, m. p. 218°, a *thiocarbamide*, m. p. 110°, and a *picrate* of its nitroso-derivative, m. p. 139°. The remaining product, 1-*cyano*-2:3-*dihydroindole* (3), is recovered from the above benzene solution as a yellow liquid, b. p. 164—168°/23 mm.   J. C. W.

Hydroxy-bases and Homologous Cholines. II. J. VON BRAUN and Z. KÖHLER (*Ber.*, 1918, **51**, 100—108. Compare A., 1916, i, 631).—2-Methyltetrahydro*iso*quinoline forms an *ethiodide*, m. p. 132—134°, which may be converted into the hydroxide. When this is distilled under reduced pressure, the chief product is o-*vinylbenzylmethylethylamine*, which has b. p. 105—107°/17 mm., and forms a *platinichloride*, m. p. 134°, and a *methiodide*, m. p. 166—167°. The reaction,
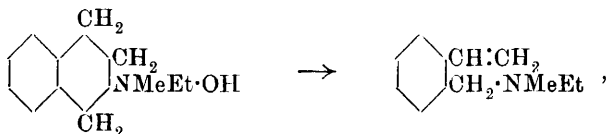
illustrates once more the instability of the tetrahydro*iso*quinoline system (A., 1917, i, 169).

N-Methyldihydro*iso*indole is formed in small quantities by the interaction of o-xylylene dibromide and methylamine. It has b. p. 81—82°/13 mm., and forms a *trihydrate*, m. p. 45—46°. Other derivatives were described by Fränkel (A., 1901, i, 44). The ethiodide (Scholtz, A., 1898, i, 568) may be converted into methylethyldihydro*iso*indylium hydroxide, which suffers decomposition in two ways on heating. The main product is *N*-methyl-dihydro*iso*indole, which is best removed by triturating the distillate with water, when the above trihydrate is formed, but o-*hydroxymethylbenzylmethylethylamine* is obtained as well, as a colourless, viscous oil, b. p. 145—150°/16 mm., which darkens on exposure to the air and gives a deep red *platinichloride*, m. p. 170°. The corresponding *dimethyldihydro*iso*indylium bromide*, m. p. 238—240°, from o-xylylene dibromide and dimethylamine, yields a hydroxide which behaves similarly on distillation. More than half of the product is o-*hydroxymethylbenzyldimethylamine*, b. p. 130—132°/13 mm., the reaction being represented thus:

$$C_6H_4{<}^{CH_2}_{CH_2}{>}NMe_2 \cdot OH \longrightarrow$$

$$C_6H_4{<}^{CH_2}_{CH_2}{>}NMe \quad \text{and} \quad C_6H_4{<}^{CH_2 \cdot NMe_2}_{CH_2 \cdot OH}.$$
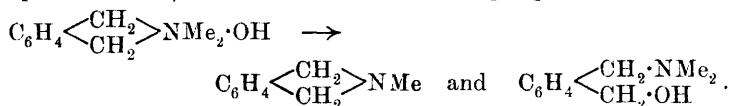
The new hydroxy-base forms an oily *picrate*, a *platinichloride*, m. p. 168°, and an oily *benzoate*, which yields a *picrate*, m. p. 159—160°, and it changes on heating with hydrochloric acid into *dimethyldihydro*iso*indylium chloride*, m. p. 198—200°.

The hydroxy-base may also be converted through the *methiodide*, m. p. 148—149°, into o-*hydroxymethylbenzyltri-*

methylammonium   chloride, $OH \cdot CH_2 \cdot C_6H_4 \cdot CH_2 \cdot NMe_3Cl$, m. p. 189°, which has exactly the same physiological activity as choline, and forms a *platinichloride,* m. p. 216°, and an *aurichloride,* m. p. 127°. The corresponding *allyliodide,* m. p. 123°, yields a chloride, which, like allylhomocholine, is antagonistic to choline.

These new hydroxy-bases and *o*-hydroxymethylbenzylpiperidine (A., 1917, i, 170) differ very characteristically from tertiary amino-benzyl alcohols of the type $OH \cdot CH_2 \cdot C_6H_4 \cdot NMe_2$ (A., 1916, i, 473, etc.). The former are colourless, the latter yellow, and whilst the latter are oxidised by formaldehyde in acid solutions, the former are quite stable towards this agent.   J. C. W.

Synthesis of Cinchonic Acids. ADOLF KAUFMANN (*Ber.,* 1918, **51**, 116—122).—The cinchonic acids or their nitriles or esters seem to be the most favourable material from which to build up synthetic alkaloids of the cinchona group. Consequently, the synthesis of these acids from quinolines is a matter of importance, and therefore some new notes on the method originated by Kaufmann in 1909 (A., 1909, i, 958) are of interest.

The conversion of quaternary salts of the quinolines into 4-cyano-1-alkyl-1 : 4-dihydroquinolines by means of cold, aqueous potassium cyanide is best carried out in the presence of ether, which removes the unstable nitrile as fast as it is formed, either by dissolving it or by causing it to crystallise out. Quinoline itself gives a 75% yield, but substituted bases give better results. Thus, the methosulphate of 6-methoxyquinoline gives a very high yield of 4-cyano-6-methoxy-1-methyl-1 : 4-dihydroquinoline, m. p. 82° (A., 1912, i, 651). With the methiodides of various nitroquinolines, extremely fine crystals of the nitrile are deposited in a very short time; 5-*nitro-4-cyano-1-methyl*-1 : 4-*dihydroquinoline,* $NO_2 \cdot C_6H_3 \Big\langle \begin{matrix} CH(CN) \cdot CH \\ NMe{-}{-}{-}CH \end{matrix}$, separates in large, pale yellow cubes or columns, m. p. 78° (decomp.); the 6-*nitro*-compound is a pale yellow, crystalline powder, m. p. 108° (decomp.); and the 8-*nitro*-compound forms large, yellow prisms, decomp. 90—92°; they all have the odour of hydrogen cyanide and are very easily oxidised, even decomposing with violence sometimes when brought from a desiccator into the air.

These nitriles may be oxidised by iodine to the methiodides of 4-cyanoquinoline (A., 1911, i, 749, 750). This is best carried out by dissolving the nitrile in pyridine and adding the solution quickly to an alcoholic solution of iodine (1 mol.). The yield of the quaternary salt varies from 90% for the unsubstituted quinoline product to 74% for the 6-methoxy-compound and 65% for the 6-ethoxy-derivative. The corresponding nitrile from hydrastinine and the above nitro-compounds react in a different way, being deprived of the cyano-group and reconverted into the parent methiodides.

The 4-cyanoquinoline methiodides are best converted into the 4-cyanoquinolines by heating alone (4-cyanoquinoline itself is

l 2

obtained in 90% yield) or with ethyl benzoate, the latter being the best treatment of the alkyloxy-derivatives.   J. C. W.

The Diketopiperazines. IV. Attempts to Prepare 2 : 3-Diketo-1-phenylpiperazine. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1686—1692. Compare A., 1916, i, 635, 672).—When an aqueous solution of 1-nitro-3 : 5-diketopiperazine ("nitroiminodiacetimide," A., 1912, i, 753) is boiled, it deposits an indigo-blue, amorphous *compound*, probably of the formula $CO<^{NH-CO}_{CH_2 \cdot NH}>C:C<^{CO-NH}_{N(NO) \cdot CH_2}>CO$. This dissolves in sodium hydroxide to give a dark reddish-brown solution, which is bleached by sodium hyposulphite.

In order to obtain soluble sulphonic acids related to this insoluble product, the authors have made many attempts, described in this and in following abstracts, to prepare 2 : 3-diketo-1-phenylpiperazine, but so far without success.

In the first place, dichlorodiacetanilide, $C_6H_5 \cdot N(CO \cdot CH_2Cl)_2$, was required. All attempts to prepare this from aniline and chloroacetyl chloride or chloroacetic anhydride resulted in the formation of the monochloroacetanilide, whilst a condensation of phenylcarbimide with chloroacetic anhydride at 160—180° gave the same product mixed with 2 : 4-diketo-3-phenyltetrahydrothiazole,

$$NPh<^{CO \cdot CH_2}_{CO \cdot S},$$
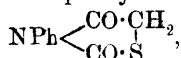
m. p. 148°.   J. C. W.

The Diketopiperazines. V. Action of Aniline on Methyl Iminodiacetate. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1692—1701).—In another attempt to prepare 2 : 3-diketo-1-phenylpiperazine, the authors have heated methyl iminodiacetate, or its hydrochloride, with aniline, in the hope of realising the reaction represented by equation (*a*). As a matter of fact, the reactions (*b*) and (*c*) are found to run concurrently.

(*a*) $NH(CH_2 \cdot CO_2Me)_2 + NH_2Ph =$
$$NH<^{CH_2 \cdot CO}_{CH_2 \cdot CO}>NPh + 2MeOH.$$

(*b*) $NH(CH_2 \cdot CO_2Me)_2 + 2NH_2Ph =$
$$NH(CH_2 \cdot CO \cdot NHPh)_2 + 2MeOH.$$

(*c*) $2NH(CH_2 \cdot CO_2Me)_2 + 2NH_2Ph =$
$$4MeOH + NHPh \cdot CO \cdot CH_2 \cdot N<^{CO \cdot CH_2}_{CH_2 \cdot CO}>N \cdot CH_2 \cdot CO \cdot NHPh.$$
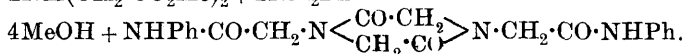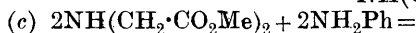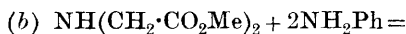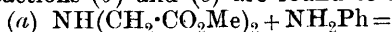
Iminodiacetonitrile (from hexamethylenetetramine and hydrogen cyanide) can be converted into methyl iminodiacetate hydrochloride in one operation (compare Jongkees, A., 1908, i, 959). 2 : 5-*Diketopiperazine*-1 : 4-*diacetanilide* (equation *c*) is not particularly soluble except in glacial acetic acid, from which it crystallises in pale grey, silky leaflets, m. p. 310—320° (decomp.). On hydrolysis, it yields the known 1 : 4-diacetic acid (*ibid.*). *Iminodiacetanilide* (*b*) is extracted from the product of the reaction by means of boiling water,

the mixture being slightly acidified by hydrochloric acid. It crystallises in glistening, long, snowy leaflets, m. p. 138—139°, the *hydrochloride* forms leaflets, m. p. 242° (decomp.), and the *nitrate*, stout needles, m. p. 182—183°. The salts are completely dissociated in water, but can be precipitated by the addition of the free acids or metallic salts in excess. The compound also reacts with acetic anhydride to give *acetyliminodiacetanilide*, m. p. 223—224°, and with absolute nitric acid to form *nitroiminodiacetotetranitroanilide*, $NO_2 \cdot N[CH_2 \cdot CO \cdot NH \cdot C_6H_3(NO_2)_2]_2$, which forms sulphur-yellow leaflets, m. p. 214—215° (decomp.), and dissolves in concentrated potassium hydroxide with blood-red colour. J. C. W.

The Diketopiperazines. VI. Action of Bromoacetamide on Glycineanilide. J. V. DUBSKY and CH. GRÄNACHER (*Ber.*, 1917, **50**, 1701—1709).—Glycineanilide,

$$NH_2 \cdot CH_2 \cdot CO \cdot NHPh, 2H_2O,$$
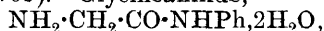
is conveniently prepared by saturating a solution of chloroacetanilide in alcohol (50 grams to 500 c.c.) with ammonia at a low temperature, heating the mixture in an autoclave at 50—60° for twelve to fifteen hours, and carefully concentrating the product. The yield is much poorer if smaller quantities are employed.

Bromoacetylglycineanilide, from bromoacetyl bromide and glycineanilide, forms slender needles, m. p. 170—172° (decomp.). It does not yield 2 : 5-diketo-1-phenylpiperazine when heated.

Reaction gradually sets in when equimolecular quantities of glycineanilide and bromoacetamide are mixed and left at 20°. The product is *triglycinediamideanilide*,

$$NHPh \cdot CO \cdot CH_2 \cdot N(CH_2 \cdot CO \cdot NH_2)_2,$$
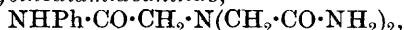
which crystallises in stout platelets, m. p. 227° (decomp.), and is not soluble in organic media. The *hydrochloride*, m. p. 200—202°, is hydrolysed by water. When heated at 200—210°/vac., the compound loses ammonia and changes into 3 : 5-*diketopiperazine*-1-*acetanilide*, $NH{<}^{CO \cdot CH_2}_{CO \cdot CH_2}{>}N \cdot CH_2 \cdot CO \cdot NHPh$, which crystallises in glistening leaflets, m. p. 189—190°, and forms a readily dissociated *hydrochloride*, $1H_2O$, leaflets, and *nitrate*, $0.5H_2O$, m. p. 124° (violent decomposition), whilst absolute nitric acid gives 3 : 5-*diketopiperazine*-1-op-*dinitroacetanilide*, very pale yellow needles, m. p. 225—226° (decomp.).

If the original glycineanilide contains iminodiacetanilide, which is usually the case, *triglycineamidedianilide*,

$$NH_2 \cdot CO \cdot CH_2 \cdot N(CH_2 \cdot CO \cdot NHPh)_2,$$
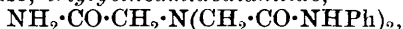
is formed as well, in the reaction with bromoacetamide. This compound is freely soluble in alcohol, and so may be extracted from the product. It crystallises in long filaments, m. p. 165°.

J. C. W.

Dyes of the Anthraquinone-2 : 1-acridone Series. FRITZ ULLMANN and PERCY DOOTSON (*Ber.*, 1918, **51**, 9—24).— Ullmann and Billig have already described the influence on the tinctorial properties of anthraquinone-2 : 1-acridone exerted by sub-

stituents in the half of the acridine system to which the anthra-
quinone residue is attached (A., 1911, i, 489, 490). The present
communication is an outcome of an inquiry into the influence of
substituents in the other part of the acridine system. The new
derivatives are generally prepared by condensing 1-aminoanthra-
quinone with the methyl ester of a substituted *o*-chlorobenzoic acid,
and then treating the corresponding free *o*-anthraquinonylamino-
benzoic acid with concentrated sulphuric acid.

Methyl o-*anthraquinonyl-1-aminobenzoate* is prepared by boiling
1-aminoanthraquinone with methyl *o*-chlorobenzoate, potassium
acetate, and a trace of copper acetate in naphthalene solution, the
yield being 92%; it crystallises in red needles, m. p. 205° (corr.),
is hydrolysed by alcoholic sodium hydroxide to the sodium salt, and
is converted by warming with concentrated sulphuric acid, or with
sodium hydroxide and hyposulphite at 40—50°, into anthraquinone-
2:1-acridone. Similarly, 1:5-diaminoanthraquinone yields *di-
methyl* o:o′-*anthraquinonyl-1*:5-*diaminodibenzoate*,

$$CO_2Me \cdot C_6H_4 \cdot NH \cdot C_6H_3 {<}^{CO}_{CO}{>} C_6H_3 \cdot NH \cdot C_6H_4 \cdot CO_3Me,$$
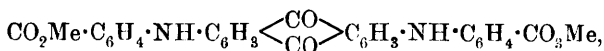
in brownish-violet, glistening crystals, m. p. 262° (corr., decomp.),
which may be converted into the corresponding acid and di-acridone
(*ibid.*).

Methyl 2-chloro-5-nitrobenzoate also condenses readily, giving an
87% yield of *methyl 5′-nitro-2′-anthraquinonyl-1-aminobenzoate*,
which crystallises in blackish-red needles, m. p. 310° (corr.), and
may be hydrolysed by *N*-sodium methoxide solution to the free
acid, orange needles, m. p. 340°. This resists condensation to an
acridone derivative, but the corresponding *5′-amino-2′-anthra-
quinonyl-1-aminobenzoic acid*, which is obtained in dark violet
crystals, m. p. 300° (decomp.), by reduction with sodium sulphide,
may be condensed by fuming sul-
phuric acid (15% SO_3) to *2′-amino-
anthraquinone-2:1-acridone* (annexed
formula). This crystallises in bluish-
violet tablets, decomp. 340°, and dyes
cotton in the vat the same shade,
whereas the unsubstituted anthra-
quinoneacridone gives reddish-violet shades.
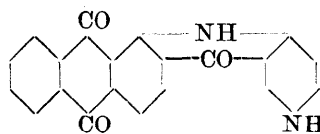
Methyl 2-chloro-5-methoxybenzoate does not react so rapidly, but
gives *methyl 2′-anthraquinonyl-1-amino-5′-methoxybenzoate*, in the
normal way. This crystallises in reddish-violet needles, m. p. 215°
(corr.), whilst the free *acid* forms a felted mass of violet needles,
m. p. 290° (decomp.), and may be converted into the chloride by
boiling with phosphorus pentachloride and benzene, and then, by
boiling with nitrobenzene, into *2′-methoxyanthraquinone-2:1-
acridone*. This forms small, violet leaflets, m. p. 308° (corr.), and
gives a hyposulphite vat of the same colour.

For the preparation of the 3′-methoxy-compound, *p*-methoxy-
anthranilic acid seemed to be the best starting material. This is
synthesised as follows: *p*-toluidine is converted into 2-nitro-*p*-tolu-

idine sulphate, then into 2-nitro-*p*-cresol; this is methylated by means of methyl sulphate, and the ether is oxidised by boiling with permanganate solution to 2-nitro-4-methoxybenzoic acid, which is reduced by means of stannous chloride. 4-Methoxyanthranilic acid (see also Friedländer, A., 1912, i, 318) is boiled with 1-chloroanthraquinone, potassium carbonate, and copper acetate in amyl alcohol, and so converted into *2'-anthraquinonyl-1-amino-4'-methoxybenzoic acid*, which crystallises in violet needles, m. p. 272° (decomp.), and may be transformed, through its chloride, into *3'-methoxyanthraquinone*-2 : 1-*acridone*. This forms a wine-red mass of felted needles, m. p. 350° (corr.), gives a red vat, and dyes cotton red. The influence of the substituent in the para-position with regard to the carbonyl group is therefore of the same order as Friedländer observed in the case of indigotins and " thioindigos " (*loc. cit.*), and as has been found in the case of 3'-chloroanthraquinone-2 : 1-acridone (D.R.-P., 245875), namely, that the shade is modified in the direction of red.

Methyl 3-chloro-2-naphthoate, m. p. 58° (for the acid, see Strohbach, A., 1902, i, 149), condenses with 1-aminoanthraquinone to form *methyl 3'-anthraquinonyl - 1 - amino - 2' - naphthoate*, violet needles, m. p. 277°, the corresponding *acid* crystallising in violet tablets, m. p. 322°. When the ester is shaken with alkaline sodium hyposulphite at 40—50° in the absence of air it gives a vat from which air precipitates *anthraquinone*-2 : 1 : 2' : 3'-*naphthacridone* (annexed formula) (for the method, see D.R.-P., 246966). This crystallises in dark violet needles, m. p. 360°, and gives a green vat, from which cotton may be dyed bluish-violet. The isomeric 2 : 1 : 1' : 2'-anthraquinonenaphthacridone of A., 1916, i, 484, and indanthrene-red B.N. extra, of D.R.-P., 237236, dye red shades. [See also *Ind.*, 178A.]   J. C. W.
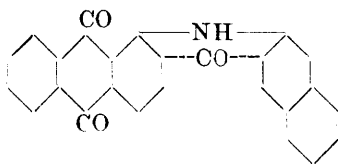
Preparation of Nitrogenous Condensation Products of the Anthraquinone Series. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 298706, 1913; from *Chem. Zentr.*, 1917, ii, 347).—Iminazole compounds of the general formula $A{<}^{NR'}_{-N}{>}CR$, where A represents an anthraquinone group possibly containing other substituents, R an aryl or alkyl radicle, and R' an aryl radicle, can be obtained in good yield with simultaneous formation of water and halogen hydracid by treating *o*-halogen substituted acylaminoanthraquinones with primary aromatic amines in the presence of neutralising agents and catalysts, such as copper salts. The products are of value for the production of dyes.

3-*Bromo*-1-N-*phenyl*-C-*phenyl*-1 : 2-*anthraquinoneiminazole*, prepared by heating 1 : 3-dibromo-2-benzoylaminoanthraquinone with aniline, potassium acetate, and copper acetate, forms yellow needles, gives an orange-red solution in sulphuric acid, and on reduction

with hyposulphite gives a vat dyeing cotton pale yellow; by warming with fuming sulphuric acid it can be converted into a sulphonic acid. 1-N-p-*Tolyl* - C - *methyl*-1 : 2-*anthraquinoneiminazole*, yellow needles, m. p. 236°, obtained similarly from 1-chloro-2-acetylamino-anthraquinone and *p*-toluidine, gives a yellow solution in sulphuric acid and a hyposulphite vat which dyes wool yellow.   D. F. T.

Chromoisomerism and Salt Formation of Iminovioluric Acids. I. I. LIFSCHITZ and LÉON KRITZMANN (*Ber.*, 1917, **50**, 1719—1738).—The bearing of residual affinity on questions of chromoisomerism and polychromism is now generally recognised, and therefore the study of a compound which can exist in tautomeric forms, and also give various internal salts by the exercise of subsidiary valencies, is of special interest. Such a compound is iminovioluric acid, which can exist, theoretically, in the following forms : —

$$CO{<}^{NH----CO}_{NH\cdot C(NH)}{>}C{:}N^{\overset{OH}{|}}$$

trans.

$$CO{<}^{NH----CO}_{NH\cdot C(NH)}{>}C{:}N_{\underset{OH}{|}}$$

cis.

$$CO{<}^{NH\cdot C(OH)}_{NH\cdot C(NH)}{>}C{\cdot}NO$$

Nitroso-enol.

$$CO{<}^{NH----CO}_{NH\cdot C(NH_2)}{>}C{\cdot}NO$$
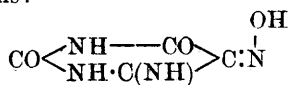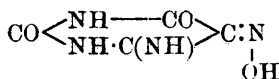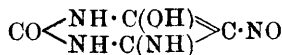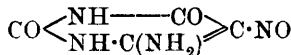
Nitroso-amino.

The isomerism in the cases of the *cis*-modification and the nitroso-amino-form would be influenced by the possibility of internal salt formation.

Iminovioluric acid is an amphoteric substance, which forms colourless salts with mineral acids and pink or red salts with the alkalis and alkaline-earths. Spectrographically, the metallic salts are identical with those of the simple violurates, which indicates that the nitroso-group is modified and involved in the establishment of a " residual affinity ring." The salts with mineral acids are optically identical with violuric acid itself, and therefore contain no residual affinity rings. The silver salt exists in a pink and a bluish-violet form, the former being most probably a salt of the above *trans*-modification, with the metallic atom linked by residual affinity to the carbonyl group, whilst the latter may be derived from the *cis*-acid, with a subsidiary valency uniting the metal and the imino-group.

The free iminovioluric acid has been isolated in three forms. The commonest is red, and spectrographically like its alkali salts; that is, it is the internally-complex form of the *cis*-modification. Another is yellowish-orange, and is to be regarded as the *trans*-isomeride, whilst the third is blue, and is most probably an internally-complex form of the nitroso-amino-type.

Some salts of iminovioluric acid were prepared by Traube in his synthesis of uric acid (A., 1900, i, 416), but the following scheme

represents an improved method: $CO(NH_2)_2 + CN \cdot CH_2 \cdot CO_2H$ (with Ac_2O) $\longrightarrow NH_2 \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot CN$.   This

$$+ NaOH \longrightarrow CO \overset{NH \text{------} CO}{\underset{NH \cdot C(NH)}{<}} CH_2$$
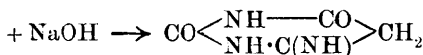
and this $+ NaNO_2 + HCl \longrightarrow$ sodium hydrogen salt of iminovioluric acid, or the normal salt, according to the conditions of the reaction.

Sodium iminoviolurate, $C_4H_3O_3N_4Na$, crystallises in silky, pink threads, and the acid salt, $C_8H_7O_6N_8Na,2\cdot5H_2O$, is reddish-violet. The *potassium* salts, obtained by similar methods, using potassium nitrite, are also pink and reddish-violet, but the acid salt has only $1H_2O$. From the sodium salt the following new salts have been prepared: *magnesium*, $MgX_2,6H_2O$, a yellow, microcrystalline powder, and MgX_2, a bright brick-red powder; *barium*, BaX_2,H_2O, red, and $Ba_3X_2,5H_2O$, pale pink; *cupric*, $CuX_2,2H_2O$, pale green, and CuX_2, almost black; *silver*, AgX,H_2O, pink, AgX, bluish-violet, and Ag_3X,xH_2O, yellow; *strychnine*, blue; *brucine*, $BX,2\cdot5H_2O$, yellow, BX, red, $BX,1\cdot5H_2O$, blue; *sulphate*, $(C_4H_4O_3N_4)_2,H_2SO_4$, colourless, m. p. 140° (loss of water); *hydrochloride*, $C_4H_4O_3N_4,HCl,H_2O$, unstable in the air. For the details of the conditions under which the various salts are formed, the original should be consulted.

Two *dimethyl* esters have also been obtained by treating the sodium salt with methyl sulphate; one is pale yellow and gives a yellow solution in sodium hydroxide, the other is orange-yellow and gives a red solution. Different ethyl esters are also formed when the different silver salts are treated with ethyl iodide.

The three forms of the free *iminovioluric acid* are obtained thus: *yellowish-orange*, by covering the sodium salt with 2- to 3-N-mineral acids; violet-tinted *red*, by exactly neutralising the sodium salt; *bluish-violet*, by boiling the others with water.

If the sodium salt is reduced with ferrous sulphate, or the free acid with iron, a very dark blue solution is obtained. In concentrated solutions, the new product may be obtained as a precipitate, which is a dark blue powder with coppery lustre. The *compound* gives a colourless solution in dilute acetic acid, from which it may be precipitated again by alkalis, and it may be represented by the formula

$$CO \overset{NH \cdot CH \text{------} O}{\underset{NH \cdot C = NH}{<}} C : NO \rightarrow Fe \cdot O \cdot Fe \leftarrow ON : C \overset{O \text{------} CH \cdot NH}{\underset{NH = C \text{---} NH}{>}} CO, 4H_2O.$$
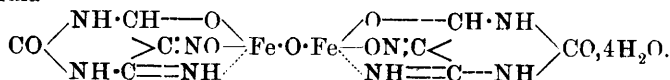
<div align="right">J. C. W.</div>

Various Observations on Phenylhydrazones, Semicarbazones, and Anils. K. VON AUWERS (*Ber.*, 1917, **50**, 1585—1614. Compare this vol., i, 27).

A. PHENYLHYDRAZONES.—Equimolecular proportions of 4-methylcoumaran-2-one and *p*-nitrophenylhydrazine hydrochloride react in aqueous-alcoholic solutions in the cold to form the normal p-*nitrophenylhydrazone* (I), which crystallises in red leaflets with metallic

green reflex, m. p. 200—204°. With an excess of the basic reagent, in boiling solutions, the coumaranone ring is opened, and the *di*-p-*nitrophenylhydrazone* of 4-*hydroxy*-m-*tolylglyoxal* (II) is formed, in dark reddish-violet leaflets, m. p. 276°.

$$C_6H_3Me \underset{O}{\overset{C:N \cdot NH \cdot C_6H_4 \cdot NO_2}{\diamondsuit}} CH_2 \longrightarrow Me \overset{C:N \cdot NH \cdot C_6H_4 \cdot NO_2}{\underset{OH}{\diamondsuit}} CH:N \cdot NH \cdot C_6H_4 \cdot NO_2$$

(I.) (II.)
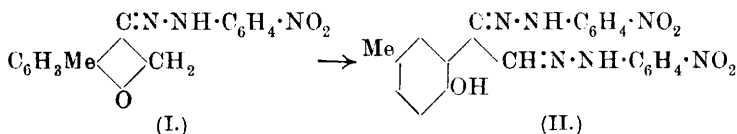
1 : 4-Dimethylcoumaran-2-one and *p*-bromophenylhydrazine combine without the elimination of water, the product being most probably the p-*bromophenylhydrazone* of 1-*hydroxy*-1 : 4-*dimethylcoumaran*-2-*one*, since it is a pale yellow powder which is not soluble in sodium hydroxide. With 1-ethoxy-1 : 4-dimethylcoumaranone and the same base in boiling alcohol, rupture of the ring takes place to a certain extent, for the *di*-p-*bromophenylhydrazone* of 4-*hydroxy*-m-*tolyl methyl diketone*, pale yellow, flat needles, m. p. 148—149°, is formed as a by-product (compare formula II or IV).

The reaction between 1 : 4-dimethylcoumaran-2-one and *p*-nitrophenylhydrazine is somewhat complicated. In the main, the ring is opened and an osazone is formed, but the mother liquors from this contain the p-*nitrophenylhydrazone* of 1-*hydroxy*-1 : 4-*dimethylcoumaran*-2-*one* (III), which forms rosettes of orange-yellow needles, m. p. 171—172°. The osazone, 4-*hydroxy*-m-*tolyl methyl diketone di*-p-*nitrophenylhydrazone*, (IV), is produced from 1 : 4-dimethylcoumaranone, or 1-hydroxy- or 1-ethoxy-1 : 4-dimethylcoumaranone by heating with *p*-nitrophenylhydrazine hydrochloride in glacial acetic acid. It crystallises in flat needles, of the appearance of chromic oxide, m. p. 255—265° (according to the rate of heating).

$$Me \overset{C:N \cdot NH \cdot C_6H_4 \cdot NO_2}{\underset{O}{\diamondsuit}} CMe \cdot OH$$

(III.)

$$Me \overset{C:N \cdot NH \cdot C_6H_4 \cdot NO_2}{\underset{OH}{\diamondsuit}} CMe:N \cdot NH \cdot C_6H_4 \cdot NO_2$$

(IV.)
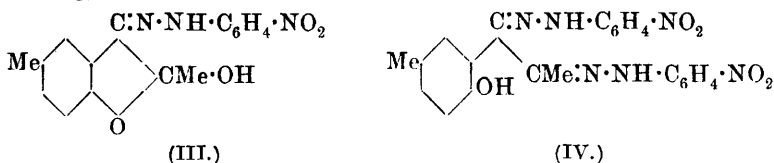
If a solution of this osazone in acetone is diluted with water or allowed to evaporate, a salmon-coloured precipitate, which looks like clean copper in the mass, is formed. This is a "*hydrate*," the elements of water being attached at one of the –C:N– groups; it has m. p. 273—274°, and loses water again if boiled with aromatic hydrocarbons or glacial acetic acid, but not by heating alone at 130°. A different "*hydrate*" is formed if the reaction between 1 : 4-dimethylcoumaranone and *p*-nitrophenylhydrazine is carried out in cold or boiling alcohol, or if 1-hydroxy-1 : 4-dimethylcoumaranone is treated with the base in boiling alcohol; this isomeride is of a bright brick-red colour, has m. p. 265—270°, and may be dehydrated more readily. A pale brick-red "*dihydrate*"

is also formed from 1-hydroxy-1:4-dimethylcoumaranone in the cold.

The colour and stability of these "hydrates" seem to depend considerably on the mode of preparation. From the analytical data, it appears that the osazone has a tendency to hold water and aromatic hydrocarbons more or less firmly, not only in chemical but also in mechanical union. It is remarkable that, of all the coumaranones, only the 1:4-dimethyl- (and 1-hydroxy-1:4-dimethyl-) compound yields these hydrates of osazones. 1-Hydroxy-1:4-dimethylcoumaran-2-one can also be converted into a normal p-*bromophenylhydrazone*, golden-yellow prisms or brilliant, sulphur-yellow needles,, m. p. 149°, and a normal p-*nitrophenylhydrazone*, slender, sulphur-yellow needles or amber-coloured, stout prisms, m. p. 176—177°.

In other cases, normal hydrazones are formed or osazones, after opening of the ring, but it frequently happens that the latter are dimorphic. Thus, 4-methyl-1-ethylcoumaran-2-one gives the *di*-p-*nitrophenylhydrazone* of 4-*hydroxy*-m-*tolyl ethyl diketone*, in orange-red needles, with blue reflex, m. p. 248—249°; occasionally, chromic oxide coloured leaflets or flat needles, possibly a "hydrate," were obtained. 4-Methyl-1-*iso*propylcoumaranone yields the *di*-p-*nitrophenylhydrazone* of 4-*hydroxy*-m-*tolyl iso*propyl *diketone*; deep orange-red crystals from much methyl alcohol, and stout, yellow prisms from glacial acetic acid, m. p. 254—255°. The difference in colour between the osazones of the ethyl and *iso*propyl tolyl diketones is remarkable. 1:3:5-Trimethylcoumaran-2-one forms a normal p-*nitrophenylhydrazone*, in orange-red needles and scales, m. p. 214—215°, when treated with the base in cold alcohol, and the di-p-nitrophenylhydrazone of 5-*hydroxy*-m-*xylyl*-4-*methyl diketone* (annexed formula),

CH$_3$ C:N·NH·C$_6$H$_4$·NO$_2$

CH$_3$ ⟨ ⟩OH CMe:N·NH·C$_6$H$_4$·NO$_2$

deep ruby-red needles, m. p. 281°, in hot solutions.
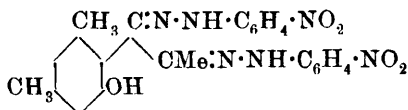
The p-nitrophenylhydrazone of benzaldehyde yields an *acetyl* derivative,

CHPh:N·NAc·C$_6$H$_4$·NO$_2$,

small, pale yellow needles, m. p. 174—175°, when treated with acetyl chloride, and the *triacetate*, OAc·CHPh·NAc·NAc·C$_6$H$_4$·NO$_2$, colourless scales, m. p. 154—155°, when warmed with acetic anhydride and a trace of concentrated sulphuric acid.

B. SEMICARBAZONES.—In this section, some cases of "hydrates" of semicarbazones are described.

1:4-Dimethylcoumaran-2-one suffers rupture of the ring when warmed with semicarbazide at 40—50°, the product being 4-*hydroxy*-m-*tolyl* α-*semicarbazidoethyl ketone semicarbazone* (I),

Me ⟨ ⟩OH C:N·NH·CO·NH$_2$ CHMe·NH·NH·CO·NH$_2$

(I.)

C$_6$H$_3$Me·OH C(OH)·NH·NH·CO·NH$_2$ CHMe·NH·NH·CO·NH$_2$
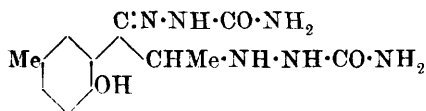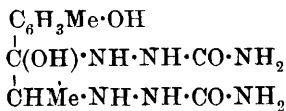
(II.)

m. p. 227°. This is precipitated as a "*hydrate*" (II), m. p. 227°, if its alkaline solutions are acidified.

1-Hydroxy-1 : 4-dimethylcoumaranone yields products, m. p. 207—210° and 227—228°, which give analytical results between the values for the true disemicarbazone of 4-hydroxy-*m*-tolyl methyl diketone and its monohydrate. 4-Methyl-1-ethylcoumaranone gives *4-hydroxy-*m-*tolyl α-semicarbazidopropyl ketone semicarbazone*, glassy, flat needles and rhombic plates, m. p. 230° (quickly heated; compare also this vol., i, 29), and its "*hydrate*," m. p. 160°. Phenyl methyl diketone forms a normal *disemicarbazone*, m. p. 229—232°.

C. ANILS.—Whilst anils show little tendency to combine with water to form "hydrates" of the type OH·CHR·NHR′, they do sometimes unite with acetic acid to form compounds of the type OH·CHR·NAcR′. Some new examples are now given.

5-Nitrosalicylaldehyde yields *5-nitrosalicylideneaniline*, yellow needles, m. p. 133°, which reacts with boiling acetic anhydride to form the *compound*,

$$OAc·C_6H_3(NO_2)·CH(OH)·NPhAc,$$
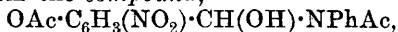
colourless needles, m. p. 145°. *5-Nitro-4-hydroxy-*m-*tolylideneaniline*, orange-red, flat needles, m. p. 133·5—134·5°, forms an *aniline* salt, stout, ruby-red prisms, and reacts with acetic anhydride to give the *compound*, $OAc·C_6H_2Me(NO_2)·CH(OH)·NPhAc$, white platelets, m. p. 167°. *5-Nitro-2-hydroxy-*m-*tolylideneaniline*, golden-yellow needles, m. p. 176—177°, forms a *diacetate*, isomeric with the last, in glistening scales, m. p. 153—154°.   J. C. W.

Diaryl-substituted Hydrazidinecarboxylic Esters and their Hydrolytic Products. Degradation of Ethyl Acetoacetate to Derivatives of Formic Acid. CARL BÜLOW and RICHARD HUSS (*Ber.*, 1918, **51**, 24—42).—The hydrolytic degradation, and other reactions, of the hydrazidinecarboxylates derived from ethyl acetoacetate (this vol., i, 42) have been studied in order to confirm the constitution assigned to them. Ethyl α-*o*-toluidinoglyoxylate 2 : 4-dichlorophenylhydrazone,

$$C_6H_3Cl_2·NH·N{:}C(NH·C_6H_4Me)·CO_2Et,$$

has been chosen for the purpose, as the possible products offer few difficulties in the way of identifying them.

I. *Proof of the Carbethoxyl Group.*—The ester is converted by contact with alcoholic ammonia into *α-*o-*toluidinoglyoxylamide 2 : 4-dichlorophenylhydrazone*,

$$C_6H_3Cl_2·NH·N{:}C(NH·C_6H_4Me)·CO·NH_2,$$

which crystallises in small needles, m. p. 152°, dissolves without change in concentrated sulphuric acid, and changes into a golden-yellow solid, with evolution of gas, if heated above its m. p. The same amide may be formed by melting the 2 : 4-dichlorophenyl-hydrazone of α-chloroglyoxylamide (A., 1913, i, 911) with *o*-toluidine.

The ester may also be converted into the *2 : 4-dichlorophenylhydrazone* of α-*o-toluidinoglyoxylhydrazide*,

$$C_6H_3Cl_2·NH·N{:}C(NH·C_6H_4Me)·CO·NH·NH_2,$$
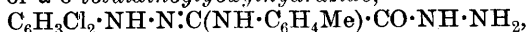
which crystallises in prisms, m. p. 145°, and condenses with aldehydes and ketones in the normal way. The iso*propylidene* compound, $C_6H_3Cl_2 \cdot NH \cdot N{:}C(NH \cdot C_6H_4Me) \cdot CO \cdot NH \cdot N{:}CMe_2$, from acetone, forms slender needles, m. p. 202°, and reacts with chlorine in cold alcoholic suspension to give 2 : 4-dichlorophenyldiazonium chloride, which later on suffers decomposition in some inexplicable manner. The *benzylidene* compound crystallises in glistening needles, m. p. 176°, and also gives 2 : 4-dichlorophenyldiazonium chloride when treated with chlorine, the product yielding a crystalline, yellowish-red dye with β-naphthol. The o-*chlorobenzylidene* compound has m. p. 198°, and apparently does not give a diazonium salt if treated with chlorine in ethereal suspension. The *salicylidene* compound forms glistening, yellow needles, m. p. 186°, and is not attacked by chlorine in light petroleum. The m-*nitrobenzylidene* compound forms glistening, pale golden-yellow needles, m. p. 229°. Ethyl diacetylsuccinate also condenses with the hydrazide, giving the 2 : 4-*dichlorophenylhydrazone* of *ethyl* 1-α-o-*toluidinoglyoxylamido*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*,

$$\begin{matrix} C_6H_3Cl \cdot NH \cdot N \\ C_6H_4Me \cdot NH \end{matrix}{>}C \cdot CO \cdot NH \cdot N{<}\begin{matrix} CMe{:}C \cdot CO_2Et \\ CMe{:}C \cdot CO_2Et' \end{matrix}$$
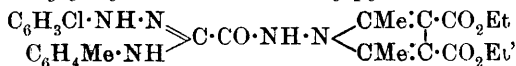
in white needles, m. p. 225°, which yields a diazonium salt with chlorine.

II. *Action of Acetic Anhydride.*—The compound readily yields an *acetyl* derivative, $C_{19}H_{19}O_3N_3Cl_2$, in colourless plates, m. p. 115°, which is also converted into a diazonium salt by chlorine.

III. *Degradation to the Hydrazidine of Formic Acid.*—The ester is wetted with alcohol and warmed with 20% potassium hydroxide at 95° for a few minutes, when a new potassium salt separates, which is dissolved in warm water and mixed with hydrochloric acid. Free α-*toluidinoglyoxylic acid* 2 : 4-*dichlorophenylhydrazone* separates as a lemon-yellow mass, which becomes dark brown in time, even in a well-closed bottle, and gives golden-yellow solutions in most solvents. It has m. p. 98°, but if kept at this temperature in an evacuated vessel, it soon loses carbon dioxide and changes into o-*toluidinoformaldehyde* 2 : 4-*dichlorophenylhydrazone*,

$$C_6H_4Me \cdot NH \cdot CH{:}N \cdot NH \cdot C_6H_3Cl_2,$$
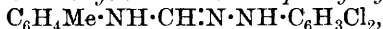
which forms white needles, m. p. 91°.

IV. *Complete Disruption.*—The ester is decomposed by warming with zinc dust and glacial acetic acid into 2 : 4-dichloroaniline and o-toluidine, this being identified by removing the solid base as far as possible and converting the oil into o-tolueneazo-β-naphthol. The ester may be recovered almost entirely unchanged after boiling with water for a week, but it is hydrolysed by boiling hydrochloric acid, yielding 2 : 4-dichlorophenylhydrazine, m. p. 90°, oxalic acid, and o-toluidine.   J. C. W.

Hydrazides and Azides of Sulphocarboxylic Acids. ERNST SCHRADER (*J. pr. Chem.*, 1917, [ii], **96**, 180—185).—When hydrazine and o-cyanobenzenesulphonyl chloride react in benzene solution, the product is a heterocyclic compound, o-*sulphohydrazido*-

benzohydrazide anhydride, $SO_2{<}{\stackrel{NH\cdot N}{C_6H_4}}{>}C\cdot NH\cdot NH_2$, needles, m. p. 154° (decomp.), which with benzaldehyde yields a *benzylidene* derivative, $C_{14}H_{12}O_2N_4S$, prisms, m. p. 179°. With aqueous sodium azide, an ethereal solution of *o*-cyanobenzenesulphonyl chloride slowly reacts with formation of o-*cyanobenzenesulphonylazide*, $CN\cdot C_6H_4\cdot SO_2\cdot N_3$, non-explosive rhombohedra, m. p. 40°.

<div align="right">D. F. T.</div>

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. VI. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1917, **101**, 15—24. Compare A., 1917, i, 711).— The ethereal extract of the products of the action of nitric acid on proteins yields, on fractional crystallisation from hot water, benzoic and *m*-nitrobenzoic acids, both of which are probably formed from the aromatic amino-acids in the protein.

From the aqueous extract of the precipitate formed by the addition of barium hydroxide and alcohol to the hydrolysed protein solution (compare A., 1915, i, 324), shining, yellow prisms separate after some days, from which, on treatment with dilute nitric acid, an *acid substance*, $C_4H_3O_4N_3$, is liberated which melts at about 300°. It appears to be a derivative of glyoxaline.

During the extraction of the products of the action of nitric acid on hæmoglobin by ether, a yellow powder gradually settles out from the originally clear liquid. On recrystallisation, an *acid substance* is obtained in small, colourless, polygonal crystals, $C_5H_3O_3N_2$, m. p. about 300°.

Among the products of the combined action of hydrochloric and nitric acids on gluten, a substance was isolated which crystallised in slender needles, but appeared, nevertheless, to be a mixture of chlorinated benzoic acids.

<div align="right">H. W. B.</div>

Effects of Electrolytes on Gelatin and their Biological Significance. I. Effects of Acids and Salts on the Precipitation of Gelatin by Alcohol. W. O. FENN (*J. Biol. Chem.*, 1918, **33**, 279—294).—The author finds that the quantity of alcohol required to precipitate a fixed amount of gelatin from its solution is dependent on the nature and number of ions present in the gelatin solution. The method consists essentially in adding 95% alcohol to 5 c.c. of the gelatin–electrolyte mixture in a test-tube until such an opacity is produced that a pencil held behind the test-tube can no longer be seen. The number of c.c. of alcohol added constitutes the " alcohol number."

The results show that acids, alkalis, and salts hinder the precipitation of gelatin by alcohol. In the case of strong acids and alkalis, this effect rapidly increases, passes through a sharp maximum, and then decreases as the concentration of the electrolyte is increased. Thus, when the conditions above described are observed, the quantity of alcohol required to precipitate the gelatin rapidly increases as the concentration of hydrochloric acid in the gelatin solution is raised from 0 to $0·024M$. From $0·024$ to $0·095M$, pre-, cipitation does not occur, however much alcohol is added, whilst

beyond this limit the amount of alcohol required slowly diminishes. When salts are added, the precipitation of the gelatin is also hindered, and the effect becomes more marked as the concentration of the salt is increased. Tervalent ions are more effective than bivalent, and bivalent than univalent in this respect. Certain salts, such as aluminium and copper chlorides, which are very effective in hindering precipitation by alcohol, resemble the strong acids in that their effect passes through a maximum and then decreases. Others, such as manganese sulphate, containing bivalent cations and anions, are exceptions to the general rule, and either assist or only very slightly hinder the precipitation of gelatin by alcohol. The effect of the sulphates, citrates, and tartrates of the alkali metals decreases in high concentrations, due to their strong "salting out" or dehydrating powers. Eventually a point is reached where the salt itself precipitates the gelatin without any addition of alcohol being required. The discussion of the theoretical significance of these results is reserved for a future communication.   H. W. B.

Action of Diazomethane on Hæmin. WILLIAM KÜSTER [with OTTO GEERING and O. KUSCH] (*Zeitsch. physiol. Chem.*, 1917, **101**, 25—32. Compare A., 1915, i, 853).—It has been stated (*loc. cit.*) that whereas bilirubin and hæmatoporphyrin are readily esterified by diazomethane, hæmin is only esterified with difficulty or not at all. Further experiments have shown that only a very small percentage of α-chlorohæmin is esterified by diazomethane, whilst α-bromohæmin is quite unattacked. On the other hand, some β-hæmin derivatives have been found to be readily methylated by this reagent. β-Bromoethylhæmin is converted into β-methyl-ethylhæmin and β-chlorohæmin into β-chloromethylhæmin; but β-chloromethylhæmin is unattacked, and in mixtures containing β-chlorohæmin and the methyl mono-ester, only the β-chlorohæmin undergoes methylation. The methylation of the second carboxyl in β-hæmin can therefore only occur through the agency of diazomethane when the first carboxyl has been esterified by the ethyl radicle, and hence it follows that the carboxyl esterified by ethyl alcohol is different from that esterified by methyl alcohol. These results furnish new evidence for the view that the carboxyl radicles in hæmin are affected in different ways by the neighbouring basic and iron-containing groups (compare A., 1912, i, 670), one being in closer relation to the basic group than the other. This is illustrated by the scheme:

$$\begin{array}{ccc} \text{COO·NH} + \text{MeOH} & \longrightarrow & \text{COO·NH} \\ \text{CO}_2\text{H} & & \text{CO}_2\text{Me} \end{array} \text{ not methylated by diazomethane}$$

$$\begin{array}{cccc} \text{COO·NH} + \text{EtOH} & \longrightarrow & \text{COO·NEt} & \\ \text{CO}_2\text{H} & & \text{CO}_2\text{H} & \end{array} \text{ methylated forming } \begin{array}{c} \text{COO·NEt} \\ \text{CO}_2\text{Me} \end{array}$$
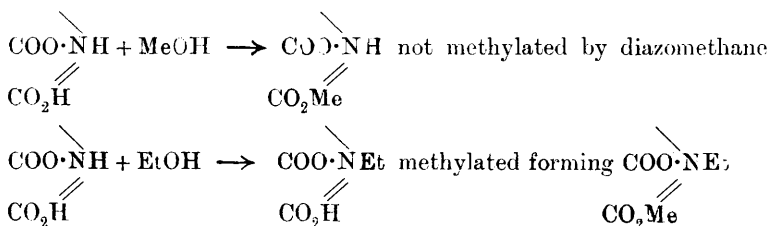
β-*Bromoethylhaemin*, $C_{36}H_{36}O_4N_4BrFe$, prepared by Mörner's method, when suspended in chloroform and treated with diazo-methane, yields β-*bromomethylethylhaemin*, $C_{37}H_{38}O_4N_4BrFe$, which is insoluble in 5% sodium carbonate solution.   H. W. B.

Esterification and Empirical Composition of Hæmin.

WILLIAM KÜSTER (*Zeitsch. physiol. Chem.*, 1917, **101**, 33—42. Compare preceding abstract).—Hæmin prepared by Mörner's method, using pure ethyl alcohol, consists of a mixture of α-hæmin and monoethylhæmin, whilst when methyl alcohol is employed, the products consist of β-hæmin, monomethyl-, and dimethyl-hæmin. When a mixture of ethyl and methyl alcohols is used, methylhæmin is first formed, which then interacts with the ethyl alcohol to form ethylhæmin. Since it has been shown (*loc. cit.*) that ethyl and methyl alcohols become attached to different carboxyl groups, it follows that the ethylhæmin formed by the direct action of ethyl alcohol on hæmin should be isomeric with that formed by the action of the mixture of alcohols in which the ethylhæmin is produced from the primary methylhæmin. Experiments carried out on these lines have not been so far successful in isolating two isomeric ethyl-hæmins, only mixtures of mono- and dialkyl-hæmins being obtained.

The analyses of the alkyl- and halogen-hæmins prepared in various ways are all in harmony with the empirical formula $C_{34}H_{32}O_4N_4Cl(Br)Fe$ for hæmin.   H. W. B.

Action of Aniline on Hæmin and its Transformation by the Acetic Acid Method.

WILLIAM KÜSTER [with, in part, LOBMILLER] (*Zeitsch. physiol. Chem.*, 1917, **101**, 43—76. Compare A., 1914, i, 887, and preceding abstracts).—The product of the action of aniline on hæmin consists of a mixture of three sub-stances. One of these, hydroxyhæmin, is formed from chloro- or bromo-hæmin by the probable intermediate production of an addi-tive compound of the hæmin with aniline, which subsequently undergoes hydrolysis. It acts as a base, forming salts with acids, and has the hydroxyl group attached directly to the iron atom in the hæmin molecule. The other two products are two dehydro-halogenohæmins, in one of which the iron atom is attached to oxygen and in the other to nitrogen. The latter N-derivative is more stable than the O-derivative, and therefore does not so readily undergo transformation into a true hæmin. By the action of aniline on β-chloromethylhæmin, N-dehydrochlorohæmin and hydroxyhæmin are formed, of which only the latter yields crystal-line β-dimethylhæmin when esterified by means of methyl alcohol and hydrogen chloride.

Two α-dehydrobromohæmins are similarly produced by the action of aniline on α-bromohæmin, and can be separated by treating with a pyridine–chloroform mixture. Part dissolves, but the solution does not yield hæmin when poured into acetic acid containing sodium chloride. The insoluble portion dissolves in alcoholic ammonia, and is readily converted into crystallised hæmin. In the first case, the iron atom is attached to nitrogen, whilst in the

second the less stable iron–oxygen compound is present, which is therefore transformable into hæmin.

In some cases, the failure to re-form a crystalline hæmin from a methylated hæmin is ascribed to the intermediate production of a "pseudohæmin," in which salt formation with one of the basic nitrogen atoms is assumed to occur. H. W. B.

The Influence of Neutral Salts on the Action of Urease. J. TEMMINCK GROLL (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 559—565).—The cations exert a preponderating influence on the decomposition of carbamide by urease, the anions having comparatively little influence. The cations and the anions, in so far as the influence of the latter can be observed, arrange themselves, as regards their retarding action on urease, in much the same order as they do in regard to their influence on various colloidal phenomena. W. G.

Physiological Chemistry.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. I. High Levels of Carbon Dioxide and Alkali. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 333—344).—The authors describe experiments on dogs which show that when, by means of subcutaneous injections of morphine, respiration is depressed and the alveolar carbon dioxide is raised, or when, by the administration of carbon dioxide in the air breathed, the carbon dioxide content of the blood is raised above the normal level, the "carbon dioxide capacity" or "alkaline reserve" (Van Slyke and Cullen, A., 1917, i, 521) of the blood also rises. This rise is probably due to a compensatory passage of alkali from the tissues into the blood. Through this mechanism, respiration exerts a powerful influence on the alkaline reserve of the blood. H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. II. Low Levels of Carbon Dioxide and Alkali induced by Ether. Their Prevention and Reversal. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 345—353. Compare preceding abstract).—The disturbance of the alkaline reserve or (as the authors prefer to call it) the carbon dioxide capacity of the blood by administration of ether appears from these experiments to be wholly dependent on disturbance of respiration. If the anæsthesia is managed so that respiration is but little increased, the lowering of the alkaline reserve of the blood is slight. When, however, respiration is simultaneously

excited, the alkaline reserve may be greatly reduced. Down to a certain critical level, recovery may spontaneously ensue, but below this level the changes appear to become irreversible, resulting in the death of the animal. Light anæsthesia loses its harmful tendencies when sufficient carbon dioxide is administered to maintain the alveolar carbon dioxide at the normal level. It follows that, in ether anæsthesia, the alkaline reserve or carbon dioxide capacity of the blood is determined and controlled by its carbon dioxide content, which is in turn dependent on the alveolar carbon dioxide, or eventually on the respiration.

When the ether anæsthesia is so profound as to depress respiration, a rise occurs in the alkaline reserve of the blood.

H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. III.   The Effects of Excessive Pulmonary Ventilation. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 355—363. Compare preceding abstracts).—The authors describe experiments on dogs which show that excessive pulmonary ventilation by means of artificial respiration induces not only a lowering of the carbon dioxide content, but also of the alkaline reserve of the blood. The arterial pressure also falls, and death may follow. If the artificial respiration, instead of being made with fresh air, is carried on by continual reinjection mainly of expired air, so that the carbon dioxide content of the blood is not reduced, the alkaline reserve and arterial pressure do not fall and the other ill-effects also fail to appear.   H. W. B.

Respiratory Regulation of the Carbon Dioxide Capacity of the Blood. IV.   The Sequence of Trauma, Excessive Breathing, Reduced Carbon Dioxide Capacity, and Shock. YANDELL HENDERSON and H. W. HAGGARD (*J. Biol. Chem.*, 1918, **33**, 365—371. Compare preceding abstracts).—The experiments show that trauma does not cause a lowering of the carbon dioxide capacity or alkaline reserve of the blood if measures are taken to prevent excessive pulmonary ventilation. Beneficial results may therefore be expected to attend the administration of carbon dioxide to wounded soldiers with the view of the prevention of "shock."

H. W. B.

The Occurrence of Creatine and Creatinine in the Blood in Normal and Pathological Conditions. II.   In Young Individuals : Method of Estimation. JOH. FEIGL (*Biochem Zeitsch.*, 1917, **84**, 264—280).—The creatinine content of blood in children up to fifteen years of age is smaller than is that of adult men. The author confirms the value of Folin's method for estimating creatinine, especially the modification of Folin and Doisy, and rejects the unfavourable criticisms of MacCrudden and Sargent. Attention is directed to the necessity of employing pure reagents.   S. B. S.

The Physical Chemistry of the White Corpuscles and Pus.
F. TANGL and K. BODON (*Biochem. Zeitsch.*, 1917, **84**, 183—193).
—Measurements of the electrical conductivity of the whole pus,
serum, and leucocytes. The conductivity of the last-named is
least. If these are diluted with water, the conductivity diminishes
progressively with the dilution, and in this respect they differ
from erythrocytes, of which the conductivity progressively increases
on dilution up to a certain point, beyond which further addition
of water causes a diminution of conductivity. S. B. S.

Phosphates in Human Blood-serum. IV. Orthophosphates and Residual Phosphorus in Bright's Disease.
JOH. FEIGL (*Biochem. Zeitsch.*, 1917, **84**, 231—245).—Attention
is directed to the differences in the distribution of phosphorus in
the serum in cases of typical (acute) and chronic glomerular
nephritis. S. B. S.

**The Change in the Hydrion Concentration of Muscle
during Work.** J. GOLDBERGER (*Biochem. Zeitsch.*, 1917, **84**,
201—209).—The reaction of extracts of muscular tissue (gastrocnemius of frogs) is always slightly acid when determined electrometrically. The hydrion concentration increases after muscular
work. The acidity, determined by titration (to phenolphthalein),
is seven to ten thousand times greater than that determined
electrometrically. The increased acidity due to muscular work is
caused chiefly by volatile acids, chiefly carbon dioxide. S. B. S.

The Reaction of Human Milk. ALEXANDER SZILI (*Biochem.
Zeitsch.*, 1917, **84**, 194—200).—The hydrion concentration of milk
is almost exactly that of water when measured electrometrically,
and does not change appreciably during the course of lactation.
The milk in the later stages of lactation requires somewhat less
alkali than in the earlier stages for neutralisation to phenolphthalein. S. B. S.

**New Constituents of Milk. III. A New Protein, Soluble
in Alcohol.** THOMAS B. OSBORNE and ALFRED J. WAKEMAN [with
CHARLES S. LEAVENWORTH and OWEN L. NOLAN] (*J. Biol. Chem.*,
1918, **33**, 243—251. Compare A., 1917, i, 103).—The new protein
is precipitated, together with caseinogen, when dilute hydrochloric
acid is added to milk. The precipitated proteins are purified by
repeatedly dissolving in dilute alkali and reprecipitating with
dilute acetic or hydrochloric acid. The moist proteins are now
treated with an equal volume of 92% alcohol; the new protein dissolves, and on pouring the concentrated filtrate into water, it
separates in flocculent masses, which can be collected on a filter,
washed, and dried over sulphuric acid. The white powder finally
obtained gives the following figures: 54·91% C, 7·17% H, 15·71% N,
0·95% S, and 0·08% P. It thus contains more carbon and sulphur
and less phosphorus than caseinogen. When examined by Haus

mann's method for the distribution of nitrogen, the new protein does not yield more amide-N or less basic-N than do caseinogen and other animal proteins, and in this respect does not resemble the alcohol-soluble proteins of vegetable origin, although so like gliadin in its solubility in relatively strong alcohol. That it is quite distinct from all the other proteins in milk is shown not only by its behaviour towards solvents and its chemical composition, but also by the fact that it does not react anaphylactically with any of these other proteins, although it is itself highly anaphylactogenic.

The alcohol-soluble milk protein possesses distinctly acid properties; it is almost insoluble in water, but dissolves in dilute alkalis. The solubility of the protein in alcohol of various degrees of concentration depends much on the temperature; it dissolves readily in warm 70% alcohol, but a small proportion separates out on cooling. It is insoluble in absolute alcohol.

Although the new protein is precipitated from its solutions by acids, it is nevertheless completely dissolved by very dilute acetic acid. On adding potassium ferrocyanide, a voluminous precipitate is produced. The protein also gives strong tryptophan, Millon's, and biuret reactions. These properties distinguish it from any type of protein hitherto discovered in animal tissues or products.

<div align="right">H. W. B.</div>

Mathematical Formulæ and Acid Excretion. GEORGE D. BARNETT (*J. Biol. Chem.*, 1918, **33**, 267—270. Compare Fitz and Van Slyke, A., 1917, i, 522).—The author raises a protest against the introduction of complex mathematical formulæ to express the relations existing between the various factors concerned in the excretion of urine by the kidney. It is shown that the results obtained by Fitz and Van Slyke, which were stated to be in agreement with the modification of Ambard's formula, plasma carbon dioxide $= 80 - \sqrt{D/W} \cdot \sqrt{C}$, can be even better expressed by the simpler formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$. Other formulæ are also put forward which express the relations between the results with a greater degree of accuracy than is attained by Fitz and Van Slyke's formula. Moreover, it is pointed out that, using Fitz and Van Slyke's formula, the average deviation of "calculated" from "found" values of plasma carbon dioxide is much greater than would result if maximal additive errors occurred in all the estimations involved.   H. W. B.

Acidosis. X. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **33**, 271—278. Compare preceding abstract).—The author agrees that the simplified formula, plasma carbon dioxide $= 80 - 5\sqrt{D/W}$, put forward by Barnett (*loc. cit.*) expresses with the greatest degree of accuracy the relationship existing between alkaline reserve and acid excretion. The additional formulæ advanced by Barnett are shown to fail when applied in the cases of children.

<div align="right">H. W. B.</div>

Physico - chemical Investigations on Experimental Uræmia. M. BIENENSTOCK and L. CSÁKI (*Biochem. Zeitsch.*, 1917, **84**, 210—224).—Dogs were rendered uræmic either by extirpation of the kidneys or by ligaturing the ureters. The following constants of the serum were determined before and after operation: dry matter, ash (soluble and insoluble in water), organic matter, surface tension, refraction, viscosity, lowering of freezing point, conductivity, hydrion concentration, nitrogen, number and volume of red corpuscles. The animals were allowed food and water after the operations, and the changes produced by the uræmia were not always in the same direction. The general results seem to warrant the conclusion, however, that uræmia causes an increase of the organic molecules in the serum and a diminution of the inorganic; the increase of the former is larger than the diminution of the latter, so that the total number of the molecules is increased. The fact of the diminution of the inorganic molecules was confirmed by estimation of chlorine in the serum of animals which had been deprived of food and water after the operation. The results are ascribed generally to the increase of the acidity of the serum produced by uræmia. S. B. S.

Pyruvic Acid. L. KARCZAG (*Biochem. Zeitsch.*, 1917, **84,** 225—230).—Both rats and guinea-pigs show a high tolerance to the acid. The injection produces neither hyperglycæmia, nor excretion in the urine of dextrose, lactic acid, volatile fatty acids, or pyruvic acid. The urine excreted is alkaline and contains a large amount of carbonate.

Certain bacteria bring about the fermentation of pyruvic acid only when grown on bouillon, but not on simpler media.

S. B. S.

Metabolic Changes induced by Administration of Guanidine Bases. I. Influence of Injected Guanidine Hydrochloride on the Sugar Content of the Blood. C. K. WATANABE (*J. Biol. Chem.*, 1918, **33**, 253—265).—The injection of guanidine hydrochloride into a rabbit is followed by symptoms which are almost identical with those of tetanus produced by extirpation of the parathyroid glands. It is now shown that hypoglycæmia results from the injection of guanidine hydrochloride, and since guanidine derivatives are known to appear in considerable amounts in the blood and urine after parathyroidectomy (Koch, A., 1913, i, 935), it is probable that the hypoglycæmia observed after the experimental removal of the parathyroids in animals (Underhill and Blatherwick, A., 1917, i, 897) or in tetanus in man is a secondary effect produced by guanidine poisoning. H. W. B.

Methods of Gas Warfare. S. J. M. AULD (*J. Washington Acad. Sci.*, 1918, **8**, 45—58).—A popular chronological account of the methods used by the Germans in gas attack. The first attack

was made by chlorine in the form of a gas cloud, this being followed by the use of phosgene [carbonyl chloride]. In gas shells, various substances were used. The original "tear" shells contained almost pure xylyl bromide or benzyl bromide, but some of the shells were rendered almost inactive by the presence of 20% of the dibromide. Later, chloromethyl and trichloromethyl chloroformates were used. They had no decided reaction on the eyes, but were highly poisonous. One of the latest substances used was dichlorodiethyl sulphide (mustard gas), which acted as a "superlachrymator." It had no immediate action on the eyes beyond causing slight irritation, but after several hours the eyes began to swell and inflame and practically to blister, the nose discharged freely, and severe coughing and even vomiting ensued. Direct contact with the spray caused severe blistering of the skin. Other substances used were: (1) in shells, allylthiocarbimide, bromomethyl ethyl ketone, methyl bromoethyl ketone, methyl dibromoethyl ketone, $CH_3 \cdot CO \cdot CHBr \cdot CH_2Br$, trichloronitromethane (chloropicrin), $CCl_3 \cdot NO_2$, diphenylchloroarsine, $AsPh_2Cl$, dichloromethyl ether, $(CH_2Cl)_2O$, phenylcarbylamine chloride, $PhN:CCl_2$; (2) in grenades, bromoacetone, bromine, chloroacetone, chlorosulphonic acid, dimethyl sulphate, methyl chlorosulphonate, sulphur trioxide.

The most satisfactory absorbents used in respirators against these attacks have been: (1) a saturated solution of sodium phenoxide; (2) hexamethylenetetramine (urotropine) used in conjunction with sodium phenoxide and sodium hydroxide; (3) active absorbent charcoal; (4) the latter and alkaline permanganate.   W. G.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Phenol in the Human Intestine.
M. RHEIN (*Biochem. Zeitsch.*, 1917, **84**, 246—263).—The author
has succeeded in isolating an organism, which he designates as
Bacterium coli phenologenes, from the human fæces which is cap-
able of producing phenol from tyrosine.   It differs in these respects
from the ordinary *coli* bacillus, to which it is similar in all other
respects.   In the presence of sugars, which are fermented by it, it
does not produce phenol.   It can also produce phenol from
p-hydroxybenzoic acid, which is thus indicated as an intermediary
product in the formation of phenol from tyrosine.   S. B. S.

**A Correlation between Bacterial Activity and Lime
Requirements of Soils.**   FIRMAN E. BEAR (*Soil Sci.*, 1917, **4**,
433—462).—Pot experiments were conducted with soils having
lime requirements varying from 0—0·23% of calcium carbonate,

the latter being applied in amounts ranging from 0·01—2·0% of the weight of the soil.   The results indicate that the various groups of soil organisms varied in their response to applications of calcium carbonate.   Ammonification proceeded fairly satisfactorily in most of the soils as obtained, but the rate was increased, in most cases, by the addition of moderate amounts of calcium carbonate. The rate of nitrification was almost directly correlated with the amount of calcium carbonate applied, and excessive applications were not injurious to the nitrifying organisms.   Nitrogen fixation by non-symbiotic soil organisms was considerably increased by the addition of calcium carbonate, but an application of monocalcium phosphate was also necessary for maximum nitrogen fixation. Nitrogen fixation accompanying the growth of soja beans took place readily in acid soils.   It was increased by small applications, but decreased by large applications of calcium carbonate.   A good growth of soja beans was obtained in a soil having a lime requirement of 0·15%, but well supplied with acid phosphate or manure. [See, further, *Ind.*, 188A.]   W. G.

The Assimilation of Carbon Dioxide. II. Baeyer's Assimilation Hypothesis. The Connecting Link in Carbohydrate Formation.

RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50**, 1777—1791.   Compare A., 1916, i, 105).—The well-known hypothesis that formaldehyde is the connecting link between carbon dioxide and carbohydrates in the plant, first suggested by Baeyer in 1870, has often been attacked in recent years. Many experiments have been made with the object of detecting formaldehyde in the plant, but even if it were found to be present it would not prove that it had been derived from carbon dioxide, since Spoehr has shown that it may be produced by the photolysis of many vegetable acids (A., 1914, i, 120).   From time to time, therefore, theories have been advanced in which other deoxidation products of carbon dioxide, such as oxalic acid and glycollic acid, have been suggested as the initial product.

On examination, it will be found that of all the possible primary products, formaldehyde is the only one in the formation of which the volume of carbon dioxide absorbed would be equal to the volume of oxygen liberated.   In other words, the "assimilatory quotient," CO_2/O_2, is 1 in the case of formaldehyde, 1·33 for glycollic acid, 2 for formic acid, and 4 for oxalic acid.   If it could be arranged, therefore, to determine this quotient in a trustworthy manner, eliminating respiratory effects and so forth, an answer could be given to the much-debated question.

By a method similar to that described in connexion with the assimilatory activity of leaves with different chlorophyll content (*loc. cit.*), the quotient can be determined with a high degree of accuracy, the experimental error only influencing the second place of decimals, and it is found that the quotient is unity, whether the temperature is 10° or 35°, whether the atmosphere is rich in carbon dioxide or even deprived of oxygen altogether (experiment with

cyclamen), or whether ordinary foliage or succulent leaves like cactus are examined.   J. C. W.

An Examination of the Leaves of Adonis Vernalis. FREDERICK W. HEYL, MERRILL C. HART, and JAMES M. SCHMIDT (*J. Amer. Chem. Soc.*, 1918, **40**, 436—453).—Tincture of *Adonis vernalis*, or false hellebore, has been used in recent years in cases of cardiac dropsy and epilepsy. The activity is usually assigned to a digitalis-like glucoside, adonidin, which was first described by Cervello (A., 1882, 1126), but the drug which may be purchased under this name is prepared from the roots (Merck's Index, 1907).

The authors have now made a systematic examination of the leaves, having obtained a considerable quantity from Leipzig. They find that an extract in 95% alcohol is somewhat more toxic than digitalis tincture, the average minimum dose which induces permanent systole of the frog's ventricle at the end of one hour (M.S.D.) being about 0·0045 c.c. per gram body weight. They have failed to obtain any more than the slightest evidence of the presence of adonidin or any glucoside in the leaf, but find that more than 60% of the toxicity is connected with the basic fraction precipitated by phosphotungstic acid.

An extract was made by the percolation of 34 kilos. of dried leaves with cold wood spirit, concentrated to a few litres in a vacuum, and mixed with twice the volume of water. The *aqueous solution* yielded: (1) an ethereal extract containing 0·45 gram of a neutral *substance*, $C_{14}H_{18}O_4$, m. p. 133°; (2) a chloroform extract containing 55 grams of indefinite material; (3) a lead acetate precipitate, from which nearly 18 grams of a lemon-yellow *acid*, $C_{31}H_{32}O_{16}$, crystallising from pyridine in plates with 1·5 mols. of solvent, and forming a *deca-acetate*, m. p. 191—192°, was recovered; *d*-glucosazone, corresponding with 1·2% of lævulose in the drug; a phosphotungstic acid precipitate, from which choline equivalent to 0·025% of the drug was recovered (this also contained the principal toxic substance, although efforts to isolate it were not successful), and 2·4% of adonitol, which is the pentitol corresponding with ribose. The *resin* yielded phytosterolin, pentriacontane, myricyl alcohol, phytosterol mixed with a lower homologue, and linolic and palmitic acids.   J. C. W.

Transformations of Inulin in the Tuber of the Jerusalem Artichoke during its Period of Rest. H. COLIN (*Compt. rend.*, 1918, **166**, 305—307).—During the winter months, the inulin is gradually converted into sucrose and levulosans, which have a lower specific rotation than inulin and are hydrolysed by invertase, and consequently are fermented by yeast.   W. G.

Organic Chemistry.

Preparation of Paraffins. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296741; from *Chem. Zentr.*, 1917, i, 611).— Alcohols are converted into their formates, and these are heated. Thus, *dihydrocholesteryl formate*, narrow tablets, m. p. 84°, when heated at 290°/10 mm., yields cholestane, and myricyl alcohol gives triacontane. The products are purified by mixing the ethereal solutions with acetic anhydride and concentrated sulphuric acid, and evaporating the ether, when the pure hydrocarbons separate.

J. C. W.

Some Reactions of Acetylene. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, **37**, 86—87T).—Iron, nickel, cobalt, and to a less extent manganese, tungsten, platinum, and palladium, react with acetylene when heated in this gas or in a mixture of the same with an inert gas. More or less carburisation of the metal results, and at the same time some of the metal enters into the soot-like deposit around the metal. This volatilisation of the metal is practically complete in the case of nickel when the heating is prolonged for a few hours; the soot contains up to 15% of nickel, whilst in experiments with iron it contains 3% of the metal. The carburisation of iron by acetylene is very rapid above 800°, and iron, nickel, and cobalt are still more rapidly carburised by a mixture of ammonia and acetylene. Iron is converted into its nitride by heating it at 800° in ammonia; the nitride when heated in acetylene loses its nitrogen, and the iron becomes highly carburised. Cadmium, zinc, lead, tin, copper, and aluminium do not react with acetylene when heated in this gas. Benzene, toluene, phenol, aniline, naphthalene, etc., behave in a similar manner to acetylene when their vapours are passed over heated nickel or iron.

W. P. S.

The Chemical Actions of the Penetrating Radium Radiation. X. The Influence of the Penetrating Rays on Chloroform and Carbon Tetrachloride. The Action of Ultraviolet Light on Chloroform. ANTON KAILAN (*Monatsh.*, 1917, **38**, 537—552. Compare Hardy and Willcock, A., 1903, ii, 622; Jorissen and Ringer, A., 1907, ii, 520).—The effect of the silent electric discharge alone (Losanitsch, A., 1910, i, 1) and in the presence of hydrogen (Besson and Fournier, A., 1910, i, 349) on chloroform has already been examined. It is now shown that the chief product of the action of the penetrating radium rays for three years on chloroform is hexachloroethane, formed probably by oxidation of the chloroform; chlorine is also produced, but almost completely disappears again by converting the chloroform into carbon tetrachloride and hydrogen chloride. During the exposure, the

chloroform became slightly turbid, and showed an alteration from $D_4^{25\cdot1}$ 1·4731 to 1·4755. With carbon tetrachloride, the density increased from D_4^{25} 1·5843 to 1·5845, and the main chemical alteration was the formation of chlorine and hydrogen chloride, the latter being produced by the action of moisture on transiently existent carbonyl chloride, which together with chlorine is produced by the action of oxygen on the carbon tetrachloride; a small quantity of hexachloroethane was also obtained, doubtless by the reaction $2CCl_4 = C_2Cl_6 + Cl_2$. A mixture of β- and γ-rays, and also γ-rays alone, produce a slight effect on chloroform, an increase in density being perceptible. The three years' exposure to the penetrating rays indicated a comparable degree of susceptibility of chloroform and carbon tetrachloride, but the total amount of decomposition in each case was less than 1%. Ultra-violet radiation exerted a similar but more rapid effect than radium radiation on chloroform; the chloroform became turbid and changed from D_4^{25} 1·4744 to 1·4762 in one day; hydrogen chloride, hexachloroethane, and an amorphous, reddish-brown solid were detected in the liquid.

<div align="right">D. F. T.</div>

Liberation of Hydrogen Chloride from Trichloroethylene.

W. ELSNER (*Chem. Zeit.*, 1917, **41**, 901—902).—In the recovery of trichloroethylene, which had been used to dissolve resin, it was found that a considerable quantity of hydrogen chloride was formed by the decomposition of the solvent. This decomposition was not brought about by the presence of metals, since the distillation was carried out in glass apparatus, and it was evidently due to the action of resin acids and a small quantity of water. The quantity of hydrogen chloride formed amounted to about 5% of the weight of the solvent.

<div align="right">W. P. S.</div>

History of Alcohol.

EDMUND O. VON LIPPMANN (*Chem. Zeit.*, 1917, **41**, 865, 883—885, 909—911).—A description of the earlier writings on the preparation of alcohol with some sixty-seven references to literature.

<div align="right">W. P. S.</div>

Alcohol and Soda Lime.

BURT H. CARROLL (*J. Physical Chem.*, 1918, **22**, 128—149).—When the vapour of ethyl alcohol is passed over soda lime heated at temperatures between 250° and 450°, reaction takes place in accordance with the equation $C_2H_5 \cdot OH + NaOH = CH_3 \cdot CO_2Na + 2H_2$. The secondary reaction, $CH_3 \cdot CO_2Na + NaOH = Na_2CO_3 + CH_4$, begins at about the same temperature, and increases so rapidly with the temperature that at 450° the acetate is decomposed almost as quickly as it is formed. It is found that the sodium hydroxide is the active constituent of the soda lime. At the temperatures used, lime was found to have but little effect on the alcohol, whereas sodium hydroxide reacts more quickly than soda lime. The advantage of using soda lime in preference to sodium hydroxide for the experiments is to be found in the fact that the hydroxide is liquid at the temperatures employed.

It is probable that the conversion of alcohol into acetate involves

three stages, in the first of which acetaldehyde is formed, the sodium hydroxide acting as catalyst. Acetaldehyde is, in fact, found amongst the products when sodium hydroxide is used. Special experiments made with acetaldehyde have shown that this is rapidly decomposed in presence of sodium hydroxide, and it is supposed that the acetaldehyde formed in the first stage is then decomposed according to the equation $CH_3 \cdot COH = CH_2\mathbin{:}CO + H_2$, with the formation of keten. The keten then reacts with the sodium hydroxide to form sodium acetate, $CH_2\mathbin{:}CO + NaOH = CH_3 \cdot CO_2Na$. The formation of keten has not actually been shown, but this is considered to be the probable course of the reaction.   H. M. D.

Preparation of Acetic Acid from Acetaldehyde. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 296282, addition to 294724; from *Chem. Zentr.*, 1917, i, 461. Compare A., 1917, i, 377).— Instead of iron compounds, such substances as nickel acetate or animal charcoal may be used as catalysts.   J. C. W.

The Scale of Influence of Substituents in Paraffin Monobasic Acids and the Correlation of Ionisation with Structure. III. The Bivalent Oxygen Atom in the ε-Position. C. G. DERICK and R. W. HESS (*J. Amer. Chem. Soc.*, 1918, **40**, 537—558).—After replying to the criticism by Wegscheider (A., 1912, ii, 529) of the "place factor" and "rule of thirds" mentioned in earlier papers (Derick, A., 1911, ii, 712; 1912, i, 188), and giving recalculated ionisation constants for various organic acids based on modern conductance units, an investigation of the ionisation constant of ε-keto-*n*-heptoic acid is described. From the determined value $1\cdot 926 \times 10^{-5}$ for the ionisation constant of this acid and a value $1\cdot 4 \times 10^{-5}$ chosen from earlier results as approximating to the ionisation constant of *n*-heptoic acid (Franke, A., 1895, ii, 252; Drucker, A., 1905, ii, 680), the "relative place influence" of the ε-ketonic oxygen atom, indicating its influence relative to that of the two corresponding hydrogen atoms in *n*-heptoic acid, is calculated to be $0\cdot 14$.

The requisite ε-keto-*n*-heptoic acid was prepared by starting from trimethylene glycol, converting this by the action of excess of hydrobromic acid into trimethylene bromide, which on reaction in methyl alcohol with a semi-molecular proportion of potassium cyanide yielded γ-bromobutyronitrile. This product was caused to undergo condensation with ethyl sodioacetoacetate, with formation of *ethyl δ-cyano-α-acetovalerate*, $CN \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHAc \cdot CO_2Et$, a colourless, viscous liquid, b. p. 154°/2 mm., accompanied by some *ethyl αη-dicyano-δ-acetyl-n-heptane-δ-carboxylate*,
$$CO_2Et \cdot CAc(CH_2 \cdot CH_2 \cdot CH_2 \cdot CN)_2,$$
a colourless solid of nutty odour, m. p. 76·5°, b. p. approx. 200°/5 mm. The former on hydrolysis with hydrochloric acid gave ethyl alcohol, carbon dioxide, ammonia, and ε-keto-*n*-heptoic acid, $CH_2Ac \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO_2H$, b. p. 181—182°/25 mm., 160°/13 mm., m. p. 36·5° (compare Perkin, T., 1890, **57**, 230; Blaise and Köhler, A., 1909, i, 204).   D. F. T.
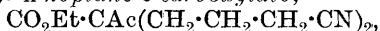
Production of Organic Compounds containing Phosphorus. J. D. RIEDEL (D.R.-P., 299992; from *Chem. Zentr.*, 1917, ii, 510).—Unsaturated hydroxy-fatty acids of high molecular weight on treatment with phosphorus trihaloids or oxyhaloids yield as primary products acid haloids in which the hydroxyl group is intact; on hydrolysis of these products with water, phosphorus derivatives of the hydroxy-acids are obtained which may be converted into the salts of the alkaline earth metals in the usual way. Ricinstearolic acid and ricinolic acid on treatment with phosphorus trichloride or tribromide yield *compounds* $C_{18}H_{33}O_5P$ and $C_{18}H_{35}O_5P$ respectively.   D. F. T.

The Formation and Decomposition of some Organic Halogenated Compounds. II. EINAR BIILMÁN (*Rec. trav. chim.*, 1918, **37**, 245—250. Compare A., 1917, i, 378).—The action of potassium iodide on dibromosuccinic acid in the presence of sulphuric acid is shown to be bimolecular, the product being fumaric acid. The reaction with *iso*dibromosuccinic acid could not be followed quantitatively, owing to the rapidity with which this acid decomposes, giving hydrogen bromide. With benzylbromomalonic acid the action is $CH_2Ph \cdot CBr(CO_2H)_2 + 3KI + H_2O = CH_2Ph \cdot CH(CO_2H)_2 + KI_3 + KBr + KOH$, but a velocity constant for the reaction could not be determined, since the iodine acted on the benzylmalonic acid formed.   W. G.

The Nature of the Inositol Phosphoric Acids of some important Feeding Materials. J. B. RATHER (*J. Amer. Chem. Soc.*, 1918, **40**, 523—536. Compare A., 1917, i, 315).—By hydrolysis of wheat bran with dilute hydrochloric acid, it is possible to obtain an acid, $C_{12}H_{41}O_{42}P_9$ or $C_6H_6(OH)(H_2PO_4)_5$, m. p. 215—216°, which can be separated from accompanying products by means of its strychnine salt, m. p. 220—222°; the latter of the two possible formulæ is preferred, and the compound is described as inositol pentaphosphoric acid; the *silver* salt is amorphous. The method described by Anderson as yielding an inositol hexaphosphoric acid (*N.Y. Geneva Expt. Sta. Tech. Bull.*, 40) is shown to give the pentaphosphoric acid as the main product. Experiments with maize, rice bran, oats, kafir corn, wheat shorts, and rice polish show the principal inositol phosphoric acid to correspond with the above composition. It is possible that other inositol phosphoric acids may be formed from these materials, but the inositol pentaphosphoric acid, together with orthophosphoric acid, constitute on the average 95% of the acid-soluble phosphorus.   D. F. T.

The Non-formation of an *o*-Tolylhydrazone of Lactose, an Affirmation of its Molecular Structure, and on its Indirect Identification. A. W. VAN DER HAAR (*Rec. trav. chim.*, 1918, **37**, 251—253).—The disaccharides, sucrose, maltose, and lactose, and the trisaccharides, trehalose and raffinose, do not yield *o*-tolylhydrazones. This result is considered to support Fischer's view as to the constitution of lactose (compare *Ber.*, 1893, **26**,

2400). Sugars, which on hydrolysis yield galactose, may be detected by hydrolysing them and preparing galactose-*o*-tolylhydrazone (compare A., 1917, ii, 515) from the hydrolysate.

W. G.

Constitution of the Disaccharides. II. Lactose and Melibiose. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1918, **113**, 188—199).—A study of the methylation of lactose, and of the hydrolysis of the product, has provided evidence which, with the previously known reactions of the disaccharide, is sufficient to establish the exact constitution of lactose and to make practically certain the structure of melibiose. Methylation is effected by means of methyl sulphate and sodium hydroxide at 30—40°, and the *heptamethyl methyllactoside* so formed yields tetramethylgalactose and a trimethylglucose on hydrolysis with 5% hydrochloric acid at 98°, these being separated by taking advantage of the fact that the former gives an insoluble anilide (Irvine, T., 1910, **97**, 1454). The trimethylglucose is stable towards permanganate, and so must be a γ-oxide; it reduces Fehling's solution, it does not form an osazone, and is not identical with Purdie and Bridgett's compound (T., 1903, **83**, 1039), which has the group –CH$_2$·OH at the end of the chain, thus limiting it to one of two isomerides.

Now, since lactose forms an osazone, and lactobionic acid yields galactose and gluconic acid on hydrolysis, it follows that the reducing group of the glucose residue is free and the adjacent hydroxyl also. The next hydroxyl must also be free, since the galacto-arabinose obtained by the degradation of lactose (Ruff and Ollendorff, A., 1900, i, 476) also forms an osazone. At the fourth carbon atom of the glucose fragment there can be no hydroxyl group, for the above trimethylglucose is γ-oxidic, and as this ether does not contain a free hydroxyl group in the sixth position, it follows that the attachment of the galactose residue to the glucose system in lactose is at the fifth carbon atom. Thus, formula I represents lactose, and, consequently, melibiose is most probably represented by formula II.

$$CH_2\text{·}OH$$

```
┌CH──────O──────ĊH          ┌CH──────O──────CH₂
│ĊH·OH         ┌ĊH          │ĊH·OH          ĊH·OH
O│ĊH·OH        │ĊH·OH       O│ĊH·OH         ┌ĊH
└ĊH           O│ĊH·OH       └ĊH            │ĊH·OH
 ĊH·OH         └ĊH·OH        ĊH·OH         O│ĊH·OH
 ĊH₂·OH                      ĊH₂·OH         └ĊH·OH
(Galactose    (Glucose
 residue.)     residue.)
      (I.)                          (II.)
```
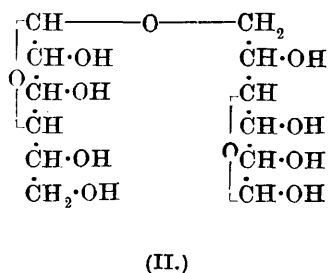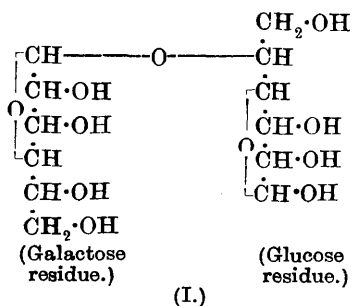
This conclusion possesses the novel feature that a disaccharide is represented as having a branched chain. It is probable that the

existence of four reducing disaccharides containing two glucose residues is to be explained on similar grounds.

[For experimental details and other arguments, see the original.]

J. C. W.

A Reinvestigation of the Cellulose–Dextrose Relationship.

MARY CUNNINGHAM (T., 1918, **113**, 173—181).—The commonly accepted opinion that cellulose is a polydextrose anhydride is based on the assumption that cellulose is quantitatively resolved into dextrose on hydrolysis. The evidence in favour of this view is not based on the isolation of dextrose in quantitative yield, but on the rotation and reducing power of the solutions (compare Willstätter and Zechmeister, A., 1913, i, 955).

It is now shown that such evidence is inadmissible, for cotton and esparto celluloses, although widely different types, give identical optical data on hydrolysis by 40% hydrochloric acid, and an acid of this concentration is known to produce constitutional changes in the simple hexoses themselves. Actual isolation and identification of the products of the hydrolysis, or simple derivatives of them, should be aimed at in such problems.

The author has therefore studied the hydrolysis of cotton and esparto cellulose by sulphuric acid dihydrate and 40% hydrochloric acid, and finds that the products are really esters of polysaccharides which contain acidic hydroxyl groups, and consequently may be isolated as barium or lead salts. No dextrose could be detected, even if the salts were heated with dilute acids, this having the effect of producing further condensation and not hydrolysis. Esparto cellulose is largely furfuroid, but the yield of furfuraldehyde obtained on distilling the diluted solution of the material is lower the longer the diluted liquid is kept, this pointing again to further condensation and not to hydrolysis.   J. C. W.

Esparto Cellulose and the Problems of Constitution.

CHARLES FREDERICK CROSS and EDWARD JOHN BEVAN (T., 1918, **113**, 182—187. Compare preceding abstract).—Esparto cellulose differs from other celluloses in giving rose-red colorations with aromatic amines and in yielding a constant high proportion (12·5%) of furfuraldehyde when decomposed by acids. It is isolated from the raw material by digesting with 17% of its weight of 3—4% sodium hydroxide at 130°, which treatment has no influence on the furfuroid content. The liquor contains, however, a colloidal furfuroid which yields as much as 50% of furfuraldehyde on boiling with hydrochloric acid. When the purified cellulose is treated with "mercerising soda" (17·5% sodium hydroxide) at 15—20°, or acetylated, or left with sulphuric acid di- or tri-hydrate, or when the concentrated, colloidal furfuroid is digested with sulphuric acid dihydrate, the furfuroid groups suffer change, for the yield of furfuraldehyde from the various products is reduced to about 7·5—8·5%. This renders doubtful the usual assumption that the furfuroids of esparto are pentosans, and coupled with the fact that

cellulose yields stable sulphates and chlorides, which hexoses and their anhydrides do not, it follows that the conception of cellulose as a complex of actual hexosan, or hexosan–pentosan, groups is no longer tenable. J. C. W.

Constitution of the Pectin Substances. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **85**, 118—161. Compare A., 1915, i, 705, 774).—The pectin substances were obtained from various fruits by treating the same first with hot alcohol and then with water at 125°. To the aqueous extract were then added alcohol and hydrochloric acid, and the pectin was precipitated as a gelatinous mass. On treatment with sodium hydroxide, scission of methyl alcohol to the extent of 7—11% takes place, and the pectin is converted into pectic acid. Pectin is soluble in water, and various preparations yielded furfuraldehyde corresponding with between 35% and 46% of arabinose and 6% and 10% of methyl pentose.

Pectic acid is sparingly soluble in hot water, giving colloidal solutions which are flocculated by salts.

Experiments on fruit jellies indicate that these owe their existence to the combined presence of sugar, pectin, and salts. The so-called bassorin of gum tragacanth also yields methyl alcohol on treatment with sodium hydroxide, and is converted into bassoric acid, which differs from pectic acid in that it is readily soluble in water. S. B. S.

Mechanism of the Electrochemical Synthesis of Carbamide. FR. FICHTER (*Zeitsch. Elektrochem.*, 1918, **24**, 41—45).—The author has carried out a number of experiments with the object of explaining the mechanism of the formation of carbamide at the anode in the electrolysis of a solution of ammonium carbonate (Drechsel, A., 1881, 192). It is shown that this synthesis can also be effected by the action of oxidising agents (ozonised oxygen, hydrogen peroxide, or calcium permanganate) on a concentrated solution of ammonium carbonate in concentrated ammonia. The hypothesis previously put forward to explain the reaction is therefore inadequate. The main change in all the reactions is the oxidation of ammonia to ammonium nitrite and nitrate. During the oxidation, at the anode or at the surface of contact with the oxidising agent, heat is set free, which is removed by external cooling to prevent loss of ammonia. This local elevation of temperature converts a portion of the ammonium carbonate into carbamide. The anodic and chemical formation of carbamide are therefore fundamentally the same as the formation in the living organism. The formation of carbamide from ammonium carbonate or ammonium carbamate is expressed by the equations

$$NH_2 \cdot CO_2 \cdot NH_4 + H_2O \rightleftharpoons (NH_4)_2CO_3 \rightleftharpoons CO(NH_2)_2 + 2H_2O.$$
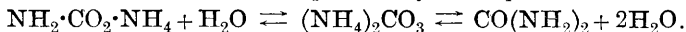
At and above 135°, ammonium carbamate cannot exist in the presence of water, consequently at this temperature and above only the right half of the equation comes into operation; with falling temperature, the equilibrium shifts to the right. Below 135°, an

increasing proportion of the ammonium carbonate is converted into the more stable carbamate, and is therefore withdrawn from the reaction if the carbonate is not stabilised by the addition of water. The lower the temperature the greater is the amount of water necessary to make the formation of carbamide possible. The best solution for carbamide formation consists of 1 mol. of ammonium carbamate and 9 mols. of water, and on the assumption that the local temperature elevation does not exceed 100°, calculations of the yield of carbamide do not contradict the hypothesis, inasmuch as the actual yields are much below the calculated values. The results show that ammonium carbonate only can be directly converted into carbamide.   J. F. S.

The Direct Conversion of Nitriles into Esters. L. SPIEGEL [with H. SZYDLOWSKY] (*Ber.*, 1918, **51**, 296—298).—The authors have found that the best conditions for the preparation of ethyl esters from nitriles are, generally speaking, treatment with one molecular proportion of concentrated sulphuric acid and ten of alcohol, at 130—140°, in a sealed tube. The lower aliphatic nitriles give equally good results, and in the aromatic series the only hindrance which is recorded is a methyl group in the ortho-position.
                                                                            J. C. W.

The Three Trichlorobenzenes and their Reaction with Sodium Methoxide. A. F. HOLLEMAN (*Rec. trav. chim.*, 1918, **37**, 195—204).—1 : 2 : 3-Trichlorobenzene, m. p. 52°, was prepared from 2 : 6-dichloro-4-nitroaniline by the following series of actions, $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_2Cl_3 \cdot NO_2 \longrightarrow C_6H_2Cl_3 \cdot NH_2 \longrightarrow C_6H_3Cl_3$, the intermediate products not being isolated.   1 : 3 : 5-Trichlorobenzene, m. p. 63°, was prepared from the same starting material by the series of actions $NO_2 \cdot C_6H_2Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_2 \cdot NO_2 \longrightarrow C_6H_3Cl_2 \cdot NH_2 \longrightarrow C_6H_3Cl_3$.   The three trichlorobenzenes were heated separately in sealed tubes at 180° with a solution of sodium methoxide, the 1 : 2 : 3-isomeride yielding 2 : 3-dichlorophenol, 2 : 6-dichlorophenol, and a certain amount of the corresponding anisoles; the 1 : 2 : 4-isomeride yielded 2 : 5-dichlorophenol with a small amount of 2 : 5-dichloroanisole, and the 1 : 3 : 5-isomeride yielded 3 : 5-dichloroanisole as the principal product with a small amount of 3 : 5-dichlorophenol. The velocity of reaction of the three trichlorobenzenes with sodium methoxide is much greater than that of the three dichlorobenzenes with the same reagent, the 1 : 3 : 5-isomeride being the most easily attacked.   W. G.

A Reaction of Aromatic Nitro-compounds. S. C. J. OLIVIER (*Rec. trav. chim.*, 1918, **37**, 241—244).—The author has examined the behaviour of twelve aromatic compounds having one or more nitro-groups in the benzene nucleus, and finds that in benzene solution they all give with aluminium bromide an orange-red coloration which disappears on the addition of water. It is suggested that the coloration is due to the loose combination of the aluminium bromide with the nitro-group. In the absence of a solvent or

on replacing the benzene by carbon disulphide, the characteristic coloration is not given in most cases. W. G.

Preparation of Derivatives of the 9 : 10-Dichloroanthracenes. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 296019; from *Chem. Zentr.*, 1917, i, 460).—The 9:10-dichloroanthracenes combine directly with nitric acid in indifferent, cold media, giving well-defined, crystalline products, probably of the formula $C_6H_4 {<} {CCl(OH) \atop CCl(NO_2)} {>} C_6H_4$. These decompose most readily, especially on warming with concentrated sulphuric acid, or organic solvents or diluents, giving anthraquinones.

Thus, 9 : 10-dichloroanthracene itself gives the above *additive* compound, which crystallises in very pale yellow needles, and decomposes at 90—95° into anthraquinone. 2 : 9 : 10-Trichloroanthracene yields a similar nitric acid compound, which gives 2-chloroanthraquinone, m. p. 204—206°, on decomposition. J. C. W.

Limits of Accuracy of Holleman's Method of Determining the Composition of a Mixture of Two or Three Isomerides. JOSEPH B. NICHOLS (*J. Amer. Chem. Soc.*, 1918, **40**, 400—403).— A method, proposed by Holleman (Die direkte Einführung von Substituenten in den Benzolkern, 1910), for the estimation of the components in a mixture of three isomerides has been submitted to examination by experiments with certain mixtures of *o*-, *m*-, and *p*-nitroanilines.

The results obtained show that the addition of *o*-nitroaniline in small quantities lowers the eutectic temperature (86·7°) which is characteristic of the binary system *m*-nitroaniline + *p*-nitroaniline to an extent which is nearly proportional to the amount of *o*-nitroaniline added. It is further found that the freezing point of p-nitroaniline is depressed by *m*-nitroaniline to an extent which is not appreciably altered when a small proportion of the *m*-nitroaniline is replaced by *o*-nitroaniline. By combining observations of the freezing point and the eutectic point, it is thus possible to estimate the proportion of *o*-, *m*-, and *p*-nitroanilines in certain mixtures of these isomerides.

The *p*-nitroaniline branch of the freezing curve for mixtures of *m*- and *p*-nitroaniline has been determined. The temperature falls from 146·99° to 97·21° when the addition of the meta-compound amounts to 48·9%. [Compare also *Ind.*, May.] H. M. D.

New Method of Preparation of Monomethylaniline and Dimethylaniline by Catalysis. ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 467—469).—Aluminium oxide is the most satisfactory catalyst for the dehydration. If the vapours of aniline and methyl alcohol in slight excess are passed over this oxide at 400—430°, a mixture of methyl- and dimethylanilines is obtained, and the methylation may be completed by further passage of the methylaniline and methyl alcohol over the catalyst. [See also *Ind.*, May.] W. G.

New Preparation of the Methyltoluidines by Catalysis.
ALPHONSE MAILHE and F. DE GODON (*Compt. rend.*, 1918, **166**, 564—566).—The method used for the preparation of methyl- and dimethyl-anilines (compare preceding abstract) is equally satisfactory for the preparation of the methyltoluidines. If the vapours of either *o*-, *m*-, or *p*-toluidine and methyl alcohol are passed over aluminium oxide at 350—400°, a mixture of methyl- and dimethyl-toluidines is obtained. A second treatment converts this mixture entirely into the tertiary base. [See also *Ind.*, May.]   W. G.

Separation of Secondary Arylamines from Primary Amines.
TUDOR WILLIAMS PRICE (*J. Soc. Chem. Ind.*, 1918, **37**, 82—84T).—The method depends essentially on the fact that the sulphates of primary amines are insoluble in the free bases, whilst those of *sec.*- and *tert.*-amines are soluble in an excess of the free amines (compare Gnehm and Blumer, *ibid.*, 1899, **18**, 129). It is particularly adaptable to the recovery of unchanged base from the mixture obtained by heating an aromatic amine with an alcohol in the presence of a condensing agent, for the quantity of primary amine to be removed is usually not excessive.

The mixture is treated with sufficient concentrated sulphuric acid to combine with the primary amine (determined by titration), when this is almost completely precipitated as sulphate. A repetition of the process may be advisable. Considerable quantities of the alkylated base are carried down with the precipitate, so this is economically washed with the alcohol employed in the reaction. The recovered alcohol and sulphate may then be used in a second charge.   J. C. W.

Production of Aromatic Selenium Compounds.
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 299510; from *Chem. Zentr.*, 1917, ii, 509—510).—Organic selenium compounds can be prepared by treating such substances as aniline, acetanilide, phenol, salicylic acid, and nitrophenol with a solution of selenium or selenium dioxide in sulphuric acid at low temperature. The product from acetanilide forms colourless crystals, m. p. approx. 260°; colourless products were also obtained from phenol, salicylic acid, and resorcinolarsinic acid, whereas aniline sulphate yielded an almost black powder and *o*- and *p*-nitrophenols yellow products. The *compound*, needles, m. p. 260° (decomp.), produced from *p*-acetylaminophenetidine had the composition

$$(OEt \cdot C_6H_3 \cdot NHAc)_3SeSO_4H, H_2O,$$
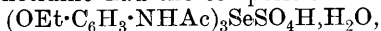
whilst antipyrine yielded a *diantipyryl selenide*, $(C_{11}H_{11}ON_2)_2Se$, colourless needles, m. p. 240° (decomp.).   D. F. T.

The Ternary System : Phenol–Acetamide–Ethyl Alcohol and the Binary System : Phenol–Benzamide. Theory of Recrystallisation.
ROBERT KREMANN and MAX WENZING (*Monatsh.*, 1918, **38**, 479—500).—When heated with phenol, acetamide and benzamide are converted into phenyl acetate and benzoate respectively, with liberation of ammonia. Doubtless intermediate

additive compounds are formed, because the fusion curve for mixtures of phenol and acetamide shows a maximum m. p. 40·8° at the composition $CH_3 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$, this result being interpreted as an indication of the presence of a free valency electron at the carbonyl and also at the amino-group of the amide. Benzamide apparently has a weaker affinity than acetamide towards phenol, the fusion curve for benzamide–phenol showing the occurrence of a compound $C_6H_5 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$, but the molten compound is dissociated to such an extent that the maximum m. p. is not observable.

The failure to obtain the compound $CH_3 \cdot CO \cdot NH_2, 2C_6H_5 \cdot OH$ by recrystallisation of a mixture of the two constituents from alcohol is attributed to the relatively low m. p. of the compound, which in the presence of a third substance, such as alcohol, may fall well below the ordinary temperature. A theoretical consideration is given of the conditions of equilibrium in a ternary system such as phenol–acetamide–alcohol, the assumption being made that there is no further formation of compounds, either binary or tertiary.

D. F. T.

Solubility of Salts of Nitrophenols in Mixtures of Alcohol and Water. W. M. FISCHER (*Zeitsch. physikal. Chem.*, 1918, **92,** 581—599).—The solubility of sodium picrate, $C_6H_2(NO_2)_3 \cdot ONa, H_2O$, in mixtures of water and ethyl alcohol at 0° and 25° varies with the composition of the solvent in a remarkable way, in that the curve shows a maximum and two minima. The maximum occurs at about 50% of alcohol by volume and the minima at about 25% and 95—99% respectively.

The anomalous form of the curve has led to the investigation of the solubility of other salts of nitrophenols, including potassium picrate, barium picrate, the sodium salts of *p*-nitrophenol, 2 : 4-dinitrophenol, and 2-chloro-4-nitrophenol, and also barium dinitrosalicylate. The results indicate that the curve is of the same type in all these cases, showing a maximum and two minima. It is suggested that the anomalous solubility curve is due to the existence of two isomeric forms of the salts, the equilibrium between which is displaced as the proportion of alcohol to water is changed. As evidence in support of this view, preliminary measurements of the extinction coefficients for solutions of salts of the nitrophenols in mixtures of ethyl alcohol and water are adduced which show that the absorption is not by any means a linear function of the composition of the solvent.

The solubility curves for potassium picrate and the sodium salt of 2 : 4-dinitrophenol exhibit a maximum in mixtures of acetone and water and a minimum in mixtures of methyl alcohol and water.

H. M. D.

The Salts of the Complex Acid : Catechol–Boric Acid. J. BÖESEKEN [with A. OBREEN and (MLLE.) A. VAN HAEFTEN] (*Rec. trav. chim.*, 1918, **37**, 184—194).—The two metallic and the ammonium salts were prepared by shaking concentrated solutions

of boric acid, catechol, and the respective hydroxide together in the molecular proportions 1 : 2 : 1. The three salts separated in the form of white leaflets. The salts of the organic bases were similarly prepared, the salts crystallising in needles. The following salts were prepared: *ammonium* salt, $(C_6H_4O_2)_3B_2O_4(NH_4)_2$; *potassium* salt, $(C_6H_4O_2)_3B_2O_4K_2$ or $(C_6H_4O_2)_3B_2O_4H_2K_2$; *rubidium* salt, analytical results not satisfactory; *aniline* salt, constitution not settled; *dimethylaniline* salt, $(C_6H_4O_2)_3BO_4H_2(C_6H_4\cdot NMe_2),5H_2O$ [?]; p-*chloroaniline* salt, $(C_6H_4O_2)_2B_3O_3(C_6H_4Cl\cdot NH_2)_3,4H_2O$ [?].

<div align="right">W. G.</div>

Methylation with Methyl Sulphate, Hydrolysis of Methyl Sulphate with Aqueous Alkali and Water in a Heterogeneous System, and a Case of Potassium Catalysis. ALFONS KLEMENC [with EMMA EDHOFER] (*Monatsh.*, 1918, **38**, 553—580). —The unequal behaviour of potassium and sodium salts has occasionally been observed, for example, in the better yield of methyl benzoate obtained by the reaction of methyl sulphate with potassium benzoate than with sodium benzoate (Graebe, A., 1905, i, 678), and the better methylation of potassium benzoate by potassium methyl sulphate than by sodium methyl sulphate. It is now shown that in the methylation of phenolic hydroxyl, for example, in quinol or resorcinol, the use of potassium hydroxide gives much poorer yields than sodium hydroxide. Physico-chemical considerations exclude the possibility that the difference is to be attributed to the different rates of diffusion of the two hydroxides from one phase to another in the heterogeneous system, and indicate that the hydrolysis occurs in a homogeneous system containing the dissolved ester. Any possible difference in the solubility of methyl sulphate in aqueous solutions of the respective alkalis is insufficient to account for the inequality in their effect. The probable explanation is that potassium hydroxide effects a more rapid hydrolysis of methyl sulphate than sodium hydroxide of equivalent concentration, on account of a catalytic influence of the undissociated potassium hydroxide molecules, in confirmation of which it is found that the addition of potassium chloride to a solution of sodium hydroxide raises the hydrolysis constant, whereas the addition of sodium chloride depresses it; on the other hand, the addition of potassium chloride to potassium hydroxide solution also depresses the hydrolysis constant. The conclusion is therefore drawn that during the methylation of a phenol, the undissociated phenoxide and the hydroxyl ions react concurrently and independently with the methyl sulphate, and that the poorer yield of methoxy-derivative obtained with the use of potassium hydroxide is due to the catalytic acceleration of the latter reaction.

<div align="right">D. F. T.</div>

6-Thiol-β-naphthol. TH. ZINCKE and R. DERESER (*Ber.*, 1918, **51**, 352—360).—The preparation of 6-thiol-β-naphthol and its more important derivatives is described (compare the 4- and 5-thiol-α-naphthols, A., 1915, i, 135, 531).

β-Naphthol-6-sulphonic acid is converted by means of ethyl chloroformate into *sodium 2-ethylcarbonatonaphthalene-6-sulphonate*, pearly leaflets, and this into the sulphonyl *chloride*, m. p. 118°, and then into *2-ethylcarbonatonaphthalene-6-sulphonanilide*, $CO_2Et \cdot O \cdot C_{10}H_6 \cdot SO_2 \cdot NHPh$, bundles of needles, m. p. 130°, which may be hydrolysed to *β-naphthol-6-sulphonanilide*, m. p. 105°. The sulphonyl chloride is reduced by means of zinc dust and hydrochloric acid to *2-ethylcarbonatonaphthalene-6-thiol*,

$$CO_2Et \cdot O \cdot C_{10}H_6 \cdot SH,$$
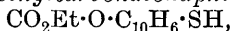
which crystallises in glistening scales, m. p. 87°, and may be reconverted into the sulphonyl chloride by treatment with chlorine. The thiol forms an *acetate*, m. p. 95°, and may be oxidised by alcoholic ferric chloride to *di-2-ethylcarbonato-6-naphthyl disulphide*, $(CO_2Et \cdot O \cdot C_{10}H_6)_2S_2$, glistening scales, m. p. 127°. It also reacts with methyl sulphate to form *2-ethylcarbonato-6-naphthyl methyl sulphide*, $CO_2Et \cdot O \cdot C_{10}H_6 \cdot SMe$, which crystallises in long, glistening needles, m. p. 97°, reacts with chlorine to form an obscure *tetrachloride*, m. p. 167—172°, and may be oxidised by means of hydrogen peroxide to the corresponding *sulphoxide*,
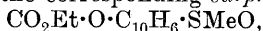
$$CO_2Et \cdot O \cdot C_{10}H_6 \cdot SMeO,$$

scales, m. p. 67°, or *sulphone*, $CO_2Et \cdot O \cdot C_{10}H_6 \cdot SMeO_2$, scales, m. p. 98°.

6-*Thiol-β-naphthol* is obtained by hydrolysing the above ethyl carbonatonaphthalenethiol. It crystallises in odourless leaflets, m. p. 137°, and forms a *diacetate*, m. p. 107°. The corresponding disulphide, methylthiol, and its sulphoxide and sulphone, are also prepared by hydrolysing the ethylcarbonato-compounds. *Di-β-naphthol-6 disulphide* forms colourless leaflets, m. p. 220—221°, and yields a *diacetate*, m. p. 167—168°; *β-naphthol-6 methyl sulphide* crystallises in silvery leaflets, m. p. 121°, forms an *acetate*, m. p. 74°, may be methylated to *2-methoxy-6-naphthyl methyl sulphide*, m. p. 105—106°, and reacts with bromine to form 1 : 5-*dibromo-β-naphthol-6 methyl sulphide*, leaflets, m. p. 194—195° (*acetate*, m. p. 145°), and the corresponding *dibromide*,

$$OH \cdot C_{10}H_4Br_2 \cdot SMeBr_2,$$
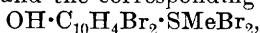
reddish-brown crystals; *β-naphtholmethyl-6-sulphoxide*,
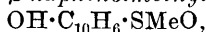
$$OH \cdot C_{10}H_6 \cdot SMeO,$$

has m. p. 164—165°, and the *sulphone*, $OH \cdot C_{10}H_6 \cdot SMeO_2$, has m. p. 151—152°, and forms an *acetate*, m. p. 145—146°, and *methyl ether*, m. p. 143—144°.

β-Naphthol-6-sulphinic acid, $OH \cdot C_{10}H_6 \cdot SO_2H$, is prepared by adding a mixture of 2-ethylcarbonatonaphthalene-6-sulphonyl chloride and sodium hydrogen carbonate to a warm solution of sodium sulphite. It crystallises in leaflets, decomp. 120—125°, and forms a methyl ester and methyl ether of this, which are identical with the above β-naphthol-6-methylsulphone and its methyl ether.

<div align="right">J. C. W.</div>

Preparation of 1 : 8-Dihydroxyanthranol. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296091; from *Chem. Zentr.*, 1917, i, 351).—1 : 8-*Dihydroxyanthranol*, m. p. 178—180°, a valuable

agent in cases of psoriasis and other skin diseases, is prepared by the reduction of 1 : 8-dihydroxyanthraquinone by means of zinc and an acid.   J. C. W.

Preparation of Acyl Derivatives of Aminonaphthols and their Sulphonic Acids. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 295767 and 296446; from *Chem. Zentr.*, 1917, i, 293, 546).—Aminonaphthols and their sulphonic acids are treated with 2-hydroxy-3-naphthoyl chloride or its acetyl derivative, giving naphthoylamino-compounds which have a great affinity for cotton and silk. Thus, 2-amino-5-naphthol-7-sulphonic acid yields 2-2′-*hydroxy-3′-naphthoylamino-5-naphthol-7-sulphonic acid*, as an almost colourless, crystalline mass, which is fixed by cotton in an alkaline solution or by silk in acetic acid solution, and may be coupled with diazonium salts on the fibre. *2-2′-Hydroxy-3′-naphthoylamino-8-naphthol-6-sulphonic acid*, *1-2′-hydroxy-3′-naphthoylamino-8-naphthol-3 : 6-disulphonic acid*, *1-2′-acetoxy-3′-naphthoylamino-7-naphthol*, m. p. 198—200°, and *1-2′-hydroxy-3′-naphthoylamino-7-naphthol*, m. p. 198—200°, are pale grey, crystalline masses or powders.   J. C. W.

d-**Benzylidenecampholic Acid.** HANS RUPE and ALFRED BLECHSCHMIDT (*Ber.*, 1918, **51**, 170—180).—A revision of the work on the action of hydrobromic acid on *d*-benzylidenecamphor described by Haller and Minguin (A., 1900, i, 452).

Benzylidenecamphor is conveniently prepared by treating camphor with sodium in toluene solution, and then adding benzaldehyde and gently boiling in a current of hydrogen. When heated in a pressure bottle at 100° with a solution of hydrogen bromide in slightly diluted acetic acid, saturated at 0°, it is converted into a crystalline acid mixed with a viscous substance. These are separated by boiling with magnesium oxide and water, the viscous substance being chiefly a non-acidic wax, and not benzylidenecampholic acid, as Haller and Minguin suggested. The acid recovered from the magnesium salt is the phenylhydroxyhomocampholic acid described by the French workers, but as it loses water readily on boiling with formic acid, it is supposed to be represented more correctly by the alternative formula,

$$CO_2H \cdot C_8H_{14} \cdot CH(OH) \cdot CH_2Ph.$$
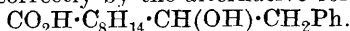
It crystallises from diluted acetic acid in thickly interwoven, stout needles, m. p. 206°, and forms an *ethyl* ester, long needles, m. p. 104°.

d-Benzylidenecampholic acid, $CO_2H \cdot C_8H_{14} \cdot CH{:}CHPh$, is the product of the action of formic acid on the hydroxy-acid. It is purified by distillation, followed by crystallisation from acetic acid (4 acid to 1 water), and is then obtained in asbestos-like masses, m. p. 124—125°, b. p. 228°/11 mm., which yield benzoic and camphoric acids on oxidation with permanganate. The *methyl* ester forms large, star-like groups of needles, m. p. 97·5—98°, and the *ethyl* ester small, glistening prisms, m. p. 95—97°; these are prepared from the chloride, which is obtained by the action of

thionyl chloride. The acid may be hydrogenated in the presence of nickel or colloidal palladium, d-*benzylcampholic acid* being obtained in slender needles, m. p. 119—119·5°, and its *methyl* ester in long, flat needles, m. p. 44°, b. p. 196—197°/13 mm. It also combines with bromine to form *αβ-dibromobenzylcampholic acid*, $CO_2H \cdot C_8H_{14} \cdot CHBr \cdot CHPhBr$, long needles, m. p. 161°, and with hydrogen bromide in glacial acetic acid to form *α-bromobenzyl-campholic acid*, $CO_2H \cdot C_8H_{14} \cdot CHBr \cdot CH_2Ph$, which crystallises in groups of spiky needles, m. p. 139°, and is also produced in excellent yield when benzylidenecamphor is left for four months with a saturated solution of hydrogen bromide in glacial acetic acid.

J. C. W.

Some Stereoisomerides of Benzylidenementhone Hydrocyanide [Phenylmenthylacetonitrile ; Phenylmenthylcyanomethane]. Eyvind Boedtker (*Bull. Soc. chim.*, 1918, [iv], **23**, 64—70).—The author has isolated seven stereoisomeric phenylmenthylacetonitriles from the products of the action of potassium cyanide on benzylidenementhone hydrochloride in alcoholic solution (compare A., 1916, i, 51). They have respectively the following properties: (1) slender, yellow needles, m. p. 193°, $[α]_D^{24} - 83°23'$ (in benzene) ; (2) colourless prisms, m. p. 158°, inactive ; (3) colourless prisms, m. p. 148°, $[α]_D^{26} + 78°7'$ (in benzene) ; (4) colourless plates, m. p. 124°, $[α]_D^{26} - 53°32'$; (5) silky needles, m. p. 183°, $[α]_D^{26} - 58°51'$; (6) slender needles, m. p. 201°, inactive ; (7) long needles, m. p. 205°, inactive. If in the preparation of these compounds the reagents are only heated in boiling alcoholic solution for one hour, the main product is the isomeride (1), but if the time of heating is prolonged or a little potassium hydroxide is introduced, the main product is the stable stereoisomeride (6), m. p. 201°.

W. G.

A New Synthesis of Tropic Acid. E. Müller (*Ber.*, 1918, **51**, 252—255).—All syntheses of tropic acid so far attempted have started from compounds, such as acetophenone, in which the :CPh·CH₂· grouping is pre-existent. None of the successful methods can be regarded as simple, but the other alternative, using a compound with the ·CHPh·CO₂R grouping, is now found to be a most convenient synthesis, which may perhaps be applied to substituted tropic acids.

Ethyl phenylacetate and ethyl formate are condensed in the presence of sodium to form the well-known mixture of desmotropic ethyl formylphenylacetates, and this mixture is reduced by means of aluminium amalgam in moist ether. About half of the formylphenylacetate combines with the sludge of aluminium hydroxide, and can only be recovered after shaking this with dilute sulphuric acid. The ethyl tropate present in the ethereal solution is hydrolysed by warm barium hydroxide solution.   J. C. W.

The Benzoylated Cyanohydrins from Aldehydes and Ketones, and the Corresponding Amides and Acids. J. Aloy and Ch. Rabaut (*Bull. Soc. chim.*, 1918, [iv], **23**, 98—101).—By

the methods previously described (compare A., 1912, i, 462; 1913, i, 620, 728; 1916, i, 263), the following benzoylcyanohydrins and the corresponding amides and acids have been obtained.

α-Benzoyloxy-γ-phenyl-Δβ-butenonitrile, CHPh:CH·CH(OBz)·CN, m. p. 66—67°, gives the *amide*, CHPh:CH·CH(OBz)·CO·NH₂.

α-Benzoyloxy-p-isopropylphenylacetonitrile,

$$\text{CHMe}_2\text{·}C_6H_4\text{·CH(OBz)·CN,}$$

m. p. 65°, gives the corresponding *amide*, m. p. 182°, which on hydrolysis yields *p-iso*propylphenylglycollic acid.

1-Benzoyloxycyclopentane-1-carboxylonitrile, OBz·C₅H₈·CN, m. p. 52—53°, giving the *amide*, OBz·C₅H₈·CO·NH₂, m. p. 111—112°.

The cyanohydrin from heptaldehyde was not isolated, but the oily product, when hydrolysed with dilute sulphuric acid, yielded the *amide*, CH₃·[CH₂]₅·CH(OBz)·CO·NH₂, m. p. 104—105°.

αβ-Dibenzoyloxysuccinonitrile, OBz·CH(CN)·CH(OBz)·CN, m. p. 195—196°, did not yield an amide, but tartaric acid was isolated from the products of hydrolysis. W. G.

New Galloyl Derivatives of Dextrose and Comparison of them with Chebulic Acid.

EMIL FISCHER and MAX BERGMANN (*Ber.*, 1918, **51**, 298—320).—Tri- and mono-galloylglucose have been obtained by means of glucosemonoacetone and glucosediacetone, a method by which partly acylated glucoses have been prepared already (A., 1916, i, 363). These derivatives have been compared very thoroughly with chebulic acid, which is known to yield gallic acid and dextrose on hydrolysis, but the conclusion is drawn that the acid is not related in structure to the galloylglucoses.

Glucosemonoacetone is treated with triacetylgalloyl chloride (this vol., i, 173) and quinoline, diluted with chloroform, and thus converted into *tri-triacetylgalloylglucosemonoacetone*,

$$\text{CMe}_2\text{:}C_6H_7O_6[\text{CO·}C_6H_2(\text{OAc})_3]_3,$$
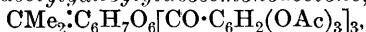
which is a faintly reddish-yellow powder, $[\alpha]_D^{20} - 66\cdot5°$ (in acetone). This is shaken at below 20°, in a current of hydrogen, with dilute sodium hydroxide, alcohol, and ether until solution takes place, when the mixture is exactly neutralised, giving *trigalloylglucosemonoacetone* as an amorphous, leafy mass, $[\alpha]_D^{21} - 93\cdot32°$ (in acetone). Dilute solutions of the derivative give deep bluish-violet colours with ferric chloride, and form precipitates with gelatin, brucine, quinine, quinoline, and pyridine. The hydrolytic scission of the *iso*propylidene group is effected by means of 0·5*N*-sulphuric acid at 70°, *trigalloylglucose* being obtained as a tannin-like mass, $[\alpha]_D^{20} - 118\cdot6°$ (in acetone), which is bitter and astringent in taste, whereas chebulic acid is sweet, and soluble in ice-cold water, whilst Chinese tannin is very sparingly soluble. A 10% alcoholic solution forms a jelly with 10% acoholic arsenic acid, and towards ferric chloride and bases it behaves like its acetone compound.

The methylcarbonato-derivative of galloyl chloride gives *tri-3 : 4 : 5-trimethylcarbonatobenzoylglucoseacetone*,

$$\text{CMe}_2\text{:}C_6H_7O_6[\text{CO·}C_6H_2(\text{O·CO}_2\text{Me})_3]_3,$$
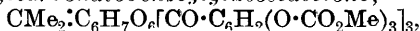
in amorphous flocks, $[\alpha]_D^{23} - 56\cdot25°$ (in *s.*-tetrachloroethane).

Similarly, the methyl ether yields *tri-3 : 4 : 5-trimethoxybenzoyl-glucoseacetone*, as a colourless powder, $[\alpha]_D^{25} - 89 \cdot 30°$ (in acetone), which does not give a colour with ferric chloride, and may be hydrolysed in the cold by means of concentrated hydrochloric acid dissolved in glacial acetic acid to form *tri-3 : 4 : 5-trimethoxy-benzoylglucose*, $C_6H_9O_6[CO \cdot C_6H_2(OMe)_3]_3$, $[\alpha]_D^{20} - 92 \cdot 99°$ (in acetone). The presence of two free hydroxyl groups in the glucose residue of this may be demonstrated by means of *p*-bromobenzoyl chloride, which, in the presence of quinoline, yields *di-p-bromo-benzoyltri-3 : 4 : 5-trimethoxybenzoylglucose*, a leafy mass, with $Br = 14 \cdot 17\%$. Trigalloylglucose reacts with diazomethane to give an indefinite methyl derivative, which also reacts with *p*-bromobenzoyl chloride, and as the product contains about 16·8% of bromine, it follows that at least two hydroxyl groups are left unattacked by the reagent. Chebulic acid behaves differently (see below).

Glucosediacetone yields *triacetylgalloylglucosediacetone*,

$$C_6H_7O_6(CMe_2)_2[CO \cdot C_6H_2(OAc)_3]_3,$$
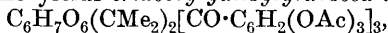
in colourless flocks, $[\alpha]_D^{18} - 30 \cdot 13°$ (acetone), from which *galloylglucosediacetone*, $[\alpha]_D^{18} - 33 \cdot 82°$, *galloylglucosemonoacetone*, $[\alpha]_D^{20} - 20 \cdot 22°$, and *galloylglucose*, $C_6H_{11}O_6 \cdot CO \cdot C_6H_2(OH)_3$, $[\alpha]_D^{18} + 46 \cdot 5°$ (alcohol), may be obtained as amorphous masses in the usual way. The behaviour of these towards the tannin reagents is described. Galloylglucose gives a deep blue colour with ferric chloride, but does not form precipitates with gelatin or bases. It is not identical with Feist's glucogallic acid (A., 1914, i, 195).

Chebulic acid, the eutannin of commerce, crystallises well from diluted acetone in needles. That it yields dextrose on hydrolysis with *N*-sulphuric acid has now been proved by the isolation of the osazone and by the fermentation method, but the cleavage proceeds at a much slower rate than is the case with the tri- and penta-galloylglucoses. A methylated chebulic acid may be obtained by the action of diazomethane (compare Richter, A., 1913, i, 989), but the product given by this when treated with *p*-bromobenzoyl chloride only contains about 9% of bromine. Chebulic acid therefore differs from trigalloylglucose. Furthermore, chebulic acid does not condense with acetone under the influence of hydrogen chloride, whereas tribenzoylglucose does so quite readily.

Tribenzoylglucose reacts in some way with diazomethane, but not to form a methylglucoside, for the product still reduces Fehling's solution. Apparently, also, it does not form an ether, for treatment with *p*-bromobenzoyl chloride, as above. indicates the presence of two free hydroxyl groups. J. C. W.

Partial Acylation of Polyhydric Alcohols and Sugars. IV. Derivatives of *d*-Glucose and *d*-Fructose. EMIL FISCHER and HARTMUT NOTH (*Ber.*, 1918, **51**, 321—352. Compare A., 1916, i, 363—365).—Hitherto, a tribenzoylglucose (*ibid.*, 364) and two stereoisomeric pentabenzoylglucoses (A., 1912, i, 888) have been

described. To these are now added a mono-, di-, and tetra-benzoyl-glucose, prepared by the application of the condensation products of dextrose with acetone. In the case of lævulose, a crystalline, monogalloyl derivative is described, and some acyl derivatives of lævuloseacetone.

Benzoylglucosediacetone, which has now been obtained crystalline, with m. p. 63—64° (corr.), $[\alpha]_D^{18}$ −49·7° (compare A., 1915. i, 118), is left with $2N$-sulphuric acid and alcohol at 50°, and thus converted into *benzoylglucosemonoacetone*, $CMe_2{:}C_6H_9O_5{\cdot}OBz$, a crystalline mass, m. p. 195—197° (corr.), $[\alpha]_D^{20}$ +8·5° (alcohol), which does not reduce Fehling's solution. This is changed into tribenzoylglucosemonoacetone (A., 1916, i, 364) by means of benzoyl chloride and quinoline, and either of the benzoylglucose-acetones may be hydrolysed by means of a mixture of sulphuric and acetic acids at 70° to give *benzoylglucose*, $C_6H_{11}O_5{\cdot}OBz,H_2O$, which forms stout, glistening crystals, m. p. 104—106° (corr.), $[\alpha]_D^{21}$ +45·76°, +44·57° after twenty-four hours (in water), $[\alpha]_D^{20}$ +47·32°, +49·34° after twenty-four hours (in alcohol). This derivative has as great a reducing power as dextrose, and suffers no weakening of this property when heated at 100° for some hours. It may be condensed with acetone to form benzoylglucosediacetone again, and it reacts with phenylhydrazine in the cold to give a *phenylhydrazone*, pale yellow prisms, m. p. 146—147° (corr.), $[\alpha]_D^{20}$ +11·1° (in pyridine), whilst it yields glucosazone if warmed with this agent.

A substance, which was presumed to be a monobenzoylglucose, is the "vacciniin" isolated by Griebel from the whortleberry (A., 1910, ii, 440). Having been supplied with some residues by Griebel, the present authors have been able to confirm the fact that the above benzoylglucose does actually occur in the natural product. They have not succeeded in isolating the substance, but have obtained a pure specimen of benzoylglucoseacetone from the crude material.

Tetrabenzoylglucose is prepared by the action of silver carbonate on benzobromo-*d*-glucose (A., 1911, i, 803) in moist acetone. An amorphous product is obtained which exhibits mutarotation, and is obviously a mixture of stereoisomerides, but an individual substance, crystallising from much light petroleum in slender needles, m. p. 119—120° (corr.), $[\alpha]_D^{21}$ +70·6° (constant; alcohol), has been isolated. This forms an additive *compound* with pyridine in equimolecular proportions, which has m. p. 103—104° (corr.) and $[\alpha]_D^{24}$ +62·07° (in alcohol).

For the preparation of a dibenzoylglucose, partly acetylated derivatives prove to be the most suitable material. Glucosediacetone is treated with acetic anhydride and pyridine at 0°, and the *acetylglucosediacetone* so formed, in platelets, m. p. 62—63°, $[\alpha]_D^{22}$ −31·5°, which tastes very bitter and does not reduce Fehling's solution, is hydrolysed by a mixture of dilute sulphuric acid and alcohol at 50° to *acetylglucosemonoacetone*, m. p. 144—146° (corr.), $[\alpha]_D^{24}$ −6·27°. This is treated with benzoyl chloride and pyridine, when *acetyldibenzoylglucoseacetone* is obtained, in elongated plate-

lets, m. p. 114—115° (corr.), $[\alpha]_D^{25} -73\cdot98°$ (acetone). When left with a mixture of $5N$-sulphuric acid and acetone at 90° in a pressure bottle, this loses not only the acetone residue, but the acetyl group as well, and *dibenzoylglucose* is formed. This crystallises from chlorobenzene in short needles or hexagonal platelets, m. p. 145—146° (corr.), $[\alpha]_D^{19}$ in alcohol, $+56\cdot2°$, $+66\cdot7°$ after six days, and reacts with *p*-bromobenzoyl chloride and pyridine to form *dibenzoyltri-p-bromobenzoylglucose*, $[\alpha]_D^9 +32°$.

Benzoylfructosediacetone is a crystalline substance, m. p. 107—108° (corr.), $[\alpha]_D^{20} -161\cdot2°$, which neither reduces Fehling's solution nor reacts with phenylhydrazine, but yields *benzoylfructosemonoacetone* when left with a mixture of acetone and N-hydrochloric acid at 50°. This is a very bitter, crystalline material which sinters at about 185°, has m. p. 202—204° (corr.) and $[\alpha]_D^{16} -151\cdot64°$, and is very sparingly soluble in water. It yields *tribenzoylfructosemonoacetone*, an amorphous solid, which may be hydrolysed to an amorphous *tribenzoylfructose*, $[\alpha]_D^{15} -249\cdot75°$, this being a powerful reducing sugar.

p-*Bromobenzoylfructosediacetone* crystallises in needles or prisms, m. p. 136—137° (corr.); *p-bromobenzoylfructosemonoacetone* has m. p. 222—225° (corr.); and *tri-p-bromobenzoylfructosemonoacetone* is a crystalline compound, with m. p. 142—143° (corr.), $[\alpha]_D^{15}$ in acetone, $-365°$.

Acetylfructosediacetone crystallises from hot water in long, glistening needles, m. p. 76—77°, $[\alpha]_D^{18} -176\cdot3°$; *acetylfructosemonoacetone* has m. p. 154—155° (corr.), $[\alpha]_D^{19} -180\cdot6°$; *triacetylfructosemonoacetone* crystallises in groups of prisms, m. p. 99—101° (corr.), $[\alpha]_D^{23} -134\cdot9°$; *benzoyldiacetylfructosemonoacetone*, m. p. 77—78°, $[\alpha]_D^{21} -132\cdot5°$, is very sparingly soluble in water, but freely so in most organic solvents; *dibenzoylacetylfructosemonoacetone* crystallises in platelets, m. p. 108—109° (corr.), $[\alpha]_D^{21} -269\cdot4°$, and has the same solubilities; and *di-p-bromobenzoylacetylfructosemonoacetone*, $CMe_2:C_6H_7O_6Ac(CO\cdot C_6H_4Br)_2$, forms large crystals, m. p. 146—147° (corr.), $[\alpha]_D^{15} -288°$.

Fructosediacetone reacts with triacetylgalloyl chloride in the presence of quinoline, giving *triacetylgalloylfructosediacetone*, which crystallises in well-developed prisms or needles, m. p. 157—159° (corr.), $[\alpha]_D^{20} -118\cdot17°$, and is hydrolysed by shaking with a mixture of alcohol and $2N$-sodium hydroxide in an atmosphere of hydrogen to *galloylfructosediacetone*, a very bitter, astringent substance, m. p. 199—200° (corr.), $[\alpha]_D^{18} -141\cdot24°$. The acetone residues may be removed in the usual way, and the product, *galloylfructose*, unlike the benzoyl derivatives, has been obtained crystalline. It forms masses of slender needles, decomp. 150—155°, $[\alpha]_D^{19}$ in water, $-80\cdot4°$, and behaves like galloylglucose towards tannin reagents, except that it gives a jelly with alcoholic arsenic acid. J. C. W.

Preparation of a 1 : 5-Dihydroxynaphthalenedicarboxylic Acid. FRANZ VON HEMMELMAYR (D.R.-P., 296035; from *Chem Zentr.*, 1917, i, 351. Compare A., 1917, i, 457).—1:5-*Dihydroxy-*

naphthalenedicarboxylic acid is a yellow powder, m. p. about 300°
(decomp.), and forms colourless alkali salts, which exhibit blue
fluorescence in water and may be easily "salted out." The acid
and its salts combine with wool fibres, subsequent treatment with
chromic acid or chromates giving very pure brown tones.

<div align="right">J. C. W.</div>

**The Mechanism of the Formation of Benzophenone by
the Friedel and Crafts' Reaction.** S. C. J. OLIVIER (*Rec. trav.
chim.*, 1918, **37**, 205—240).—A study of (1) the action of benzoyl
chloride on benzene in the presence of aluminium chloride in
benzene solution; (2) the action of benzoyl bromide on benzene in
the presence of aluminium bromide in benzene solution; (3) the
reaction (2), but in carbon disulphide as solvent. Reaction (1) is
unimolecular, and shows a slight but regular fall in the value of
K with the time. The presence of an excess of benzoyl chloride
is without influence on the reaction. One molecule of aluminium
chloride can only transform one molecule of benzoyl chloride, and
the action $COPhCl,AlCl_3 + C_6H_6 = COPh_2,AlCl_3 + HCl$ is not
reversible. Reaction (2) is also unimolecular, with a slight fall
in the value of K, but the velocity of reaction is much greater than
with the chlorides. With an excess of aluminium bromide, the
velocity of the reaction increases enormously, the excess of this
catalyst acting almost proportionately to its concentration. Cryo-
scopic measurements show that in benzene solution the compound
$COPh_2,AlBr_3$ easily forms associated molecules, the same being un-
doubtedly true of the compound $COPhBr,AlBr_3$, and these
associated molecules are notably more active than the unassociated
molecules. The reaction (3) in carbon disulphide solution may be
considered as bimolecular, with a fall in the value of K, an excess
of aluminium bromide again causing an enormous increase in the
velocity of reaction. The velocity constant also increases slightly
with an increase in the concentration of the benzene.   W. G.

Preparation of Triarylmethane Dyes, Fast to Light.
FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P., 295495;
from *Chem. Zentr.*, 1917, i, 150).—"Diarylindyl-dyes, which
contain an amino-, sulpho-, alkyloxy- or acyloxy-group in place of
the halogen atom in the para-position with regard to the methane
carbon atom, are treated with primary aromatic amines."
The following intermediate compounds are mentioned:
p-*methoxy*-p′-*dimethylaminobenzophenone*, m. p. 133°, from
p-methoxybenzanilide and dimethylaniline; p-*hydroxy*-p′-*diethyl-
aminobenzophenone*, m. p. 188°, from p-amino-p′-diethylamino-
benzophenone, which is obtained from the nitro-compound, and
this from p-nitrobenzanilide and diethylaniline; p-*dimethylamino-
benzophenone*-p′-*sulphonic acid*, from the above amine by diazotisa-
tion, treatment with sulphurous acid and copper paste, and oxida-
tion of the sulphinic acid with permanganate; p-*amino*-p′-*dimethyl-
amino*-o′-*methylbenzophenone*, m. p. 151°, by the reduction of the

product obtained from *p*-nitrobenzanilide and dimethyl-*m*-toluidine; *1-benzyl-2-methylindole*, b. p. 245°/16 mm., by melting the phenylbenzylhydrazone of acetone with zinc chloride.

<div align="right">J. C. W.</div>

The Condensation of Aldehydes with ω-Bromoaceto-phenone, and some of the Compounds obtained thereby. SVEN BODFORSS (*Ber.*, 1918, **51**, 192—214. Compare A., 1917, i, 223).—When ω-bromoacetophenone is treated with a solution of sodium ethoxide, it yields the *cis*- and *trans*-modificatiors of 2-bromo-3:4-oxido-3:5-diphenyltetrahydrofuran (A., 1913, i, 1219), but if certain aldehydes are present, condensation between the unlike molecules takes place, resulting in the formation of ethylene oxides, most probably according to the scheme $COPh \cdot CH_2Br +$

$$CHPhO = COPh \cdot CHBr \cdot CHPh \cdot OH = COPh \cdot CH {<}{\overset{CHPh}{\underset{O}{|}}} + HBr.$$
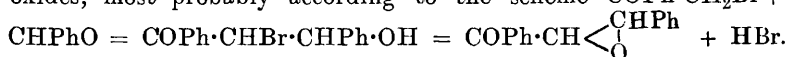
This condensation takes place particularly well if the aldehyde contains negative substituents, but negative results are usually given by aldehydes with positive substituents; thus, benzaldehyde, the nitrobenzaldehydes, *p*-chlorobenzaldehyde, bromo- and nitro-anisaldehydes, bromopiperonaldehyde, *m*-nitrocinnamaldehyde, cuminaldehyde, and terephthalaldehyde do react, whilst acet-aldehyde, *iso*butaldehyde, heptaldehyde, citraldehyde, anisaldehyde, piperonaldehyde, cinnamaldehyde, and *p*-tolualdehyde do not react with ω-bromoacetophenone. ω-Chloro-*p*-methoxyacetophenone, however, is of itself so very stable towards sodium ethoxide that even an aldehyde like anisaldehyde will condense with it in the above manner, although only slowly.

The following are new examples of the condensation of aldehydes with ω-bromoacetophenone in equimolecular proportions : *o*-nitrobenzaldehyde gives *benzoyl-o-nitrophenylethylene oxide*, rectangular prisms, m. p. 110°, and thin needles, m. p. 175° (modifications "*a*" and "*β*"); bromoanisaldehyde forms *benzoyl-3-bromo-4-methoxyphenylethylene oxide*, very long needles, m. p. 158°; nitroanisaldehyde yields *benzoyl-3-nitro-4-methoxyphenyl-ethylene oxide*, short prisms, m. p. 172—173°; bromopiperon-aldehyde gives *benzoyl-(?)-bromo-3:4-methylenedioxyphenylethylene oxide*, needles, m. p. 98—98·5°; *m*-nitrocinnamaldehyde produces *benzoyl*-m-*nitrostyrylethylene oxide*,

$$COPh \cdot CH {<}{\overset{CH \cdot CH:CH \cdot C_6H_4 \cdot NO_2}{\underset{O}{|}}},$$
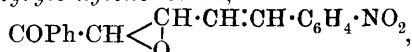
yellow crystals, m. p. 115—116°; terephthalaldehyde forms *benzoyl*-p-*aldehydophenylethylene oxide*, m. p. 116—119°.

Under the same conditions, benzoylacetone forms *α-acetyl-αβ-dibenzoylethane* (*acetyldiphenacyl*) in colourless cubes, m. p. 88—89°, which may be hydrolysed to diphenacyl, thus :

$$CHAc{:}CPh \cdot ONa + COPh \cdot CH_2Br \longrightarrow CHAcBz \cdot CH_2Bz \xrightarrow{NaOH}$$

$$CH_2Bz \cdot CH_2Bz + Ac \cdot ONa.$$
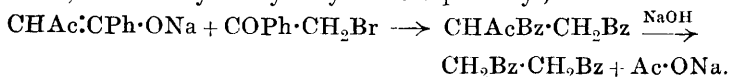
p-Chloroacetylanisole   (ω-chloro-*p*-methoxyacetophenone)   and anisaldehyde react to form *anisoylanisylethylene oxide*,

$$OMe \cdot C_6H_4 \cdot CO \cdot CH \underset{O}{\overset{CH \cdot C_6H_4 \cdot OMe}{\diagdown|}} ,$$
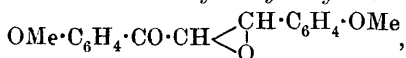
glistening, rhombic scales, m. p. 118—119°.

As has been mentioned already (*loc. cit.*), these ethylene oxides may be condensed with a further proportion of ω-bromoaceto-phenone to form dioxides. Thus, benzaldehyde may be converted into *α-benzoyl-βδ-diphenylbutadiene dioxide* (I), which crystallises in long needles, m. p. 156°. When boiled with aqueous-alcoholic potassium hydroxide, this dioxide yields *αγδ-trihydroxy-αβδ-tri-phenyl-n-valeric acid* (II), m. p. 178—179°, which forms a *tri-benzoate*, m. p. 150—150·5°. The reaction apparently follows the course indicated, thus:

$$COPh \cdot CH \overset{}{\underset{O}{\diagdown\diagup}} CPh \cdot CH \overset{}{\underset{O}{\diagdown\diagup}} CHPh \longrightarrow COPh \cdot CO \cdot CHPh \cdot CH \underset{O}{\overset{CHPh}{\diagdown|}}$$

$$CO_2H \cdot CPh(OH) \cdot CHPh \cdot CH \underset{O}{\overset{CHPh}{\diagdown|}}$$

$$CO_2H \cdot CPh(OH) \cdot CHPh \cdot CH(OH) \cdot CHPh \cdot OH$$

(II.)
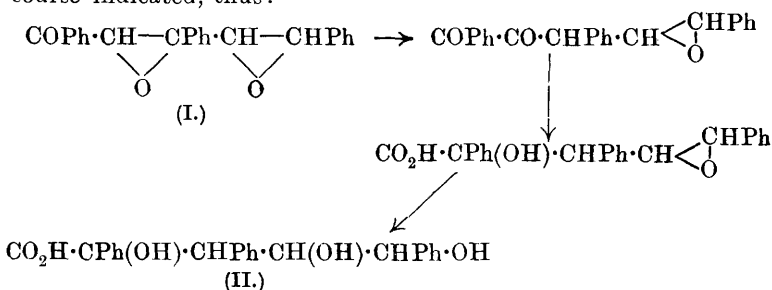
A different type of dioxide is obtained by condensing a dialdehyde with a bimolecular quantity of ω-bromoacetophenone. Thus, terephthalaldehyde gives *phenylenebisdibenzoylethylene oxide*,

$$COPh \cdot CH \overset{}{\underset{O}{\diagdown\diagup}} CH \cdot C_6H_4 \cdot CH \overset{}{\underset{O}{\diagdown\diagup}} CH \cdot COPh ,$$
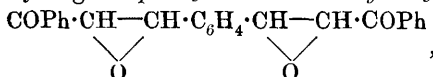
which crystallises in thin, pearly scales, m. p. 220—222°, and may be reduced by potassium iodide in glacial acetic acid to tere-phthalylidenediacetophenone, $C_6H_4(CH:CH \cdot COPh)_2$, the product being identical with that obtained by the condensation of aceto-phenone with telephthalaldehyde (see Lendenfeld, A., 1907, i, 221).

Benzoyl-*m*-nitrophenylethylene oxide reacts with stannic chloride as though it were a diketone, but the *product*, $C_{15}H_{11}O_4N,SnCl_4$, crystallising in large, yellowish-brown groups, is not identical with that given by the genuine diketonic isomeride,

$$COPh \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot NO_2.$$
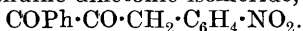
Widman has shown that benzoylphenylethylene oxide reacts with hydroxylamine under different conditions to form various com-pounds, partly oximes and partly cyclic substances (A., 1917, i, 221). Benzoyl-*m*-nitrophenylethylene oxide gives equally com-plicated reactions. When boiled with hydroxylamine hydrochloride and alcohol, it yields 3-*phenyl*-5-m-*nitrophenyl*isooxazole,

$$N \underset{O——C \cdot C_6H_4 \cdot NO_2}{\overset{CPh \colon CH}{\diagup \quad \|}} ,$$
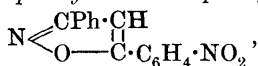
in thin tablets, m. p. 176—177°, which may also be prepared in the same way from the isomeric phenyl *m*-nitro-*a*-hydroxystyryl ketone (*loc. cit.*, 224). The mother liquor from this contains an *oxime*, "*a*," m. p. 121·5°, which is soluble in sodium hydroxide and non-reducible by hydriodic acid, and gives an *acetate*, large flakes, m. p. 132—132·5°. If the ethylene oxide is boiled with hydroxylamine hydrochloride and sodium acetate in alcohol, it yields another *oxime*, "*β*," which crystallises in slender needles, m. p. 145°, forms an *acetate*, prisms, m. p. 123°, changes into the *a*-oxime when treated with hydrochloric acid, and into a third *oxime*, "*γ*," small, glassy cubes, m. p. 153°, when crystallised from methyl alcohol, and produces 4- or 5-*hydroxy*-3-*phenyl*-5-*m*-*nitrophenyl*iso-*oxazolidine*,

$$\text{NH}{<}^{\text{CHPh·CH·OH}}_{\text{O————CH·C}_6\text{H}_4\text{·NO}_2} \quad \text{or} \quad \text{NH}{<}^{\text{CHPh·CH}_2}_{\text{O————C(OH)·C}_6\text{H}_4\text{·NO}_2},$$
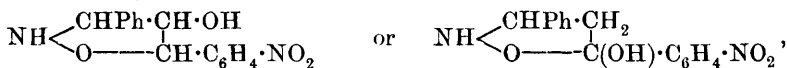
prisms, m. p. 145—146° (*nitroso*-compound, m. p. 135—140°), when boiled with potassium iodide and glacial acetic acid.

Benzoyl-*m*-nitrophenylethylene oxide reacts with semicarbazide acetate in cold alcohol to form 4-*hydroxy*-3-*phenyl*-5-*m*-*nitrophenyl*-4 : 5-*dihydropyrazole*-1-*carboxylamide*,

$$\text{NH}_2\text{·CO·N}{<}^{\text{CH(C}_6\text{H}_4\text{·NO}_2\text{)·CH·OH}}_{\text{N}========\text{CPh}},$$
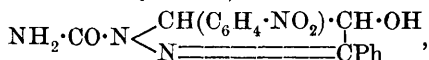
which crystallises in short prisms, m. p. 162—163° (decomp.). The same compound is given by the corresponding chlorohydrin, $\text{OH·CHBz·CHCl·C}_6\text{H}_4\text{·NO}_2$, but the isomeric phenyl *m*-nitro-*a*-hydroxystyryl ketone yields a different product, namely, the normal *semicarbazone*, $\text{NH}_2\text{·CO·NH·N:CPh·CH:C(OH)·C}_6\text{H}_4\text{·NO}_2$, m. p. 120—125° (decomp.). Similarly, the chlorohydrin usually reacts with hydrazine hydrate to form 4-*hydroxy*-3-*phenyl*-5-*m*-*nitrophenyl*-4 : 5-*dihydropyrazole*, in rhombic leaflets, m. p. 184—185°, but on one occasion 4-*hydroxy*-5-*hydrazino*-3-*phenyl*-5-*m*-*nitrophenyl*-4 : 5-*dihydropyrazole* was obtained instead, in yellow needles, m. p. 165°.

Thiocyanic acid and thiocarbamides also condense with benzoyl-*m*-nitrophenylethylene oxide, water being eliminated. Thiocyanic acid gives a *compound* which crystallises in pale yellow prisms, m. p. 120—125° (decomp.), forms an *acetyl* derivative, m. p. 111°, and is probably represented by the formula

$$\text{CO}{<}^{\text{NH·CHBz}}_{\text{S——CH·C}_6\text{H}_4\text{·NO}_2}.$$
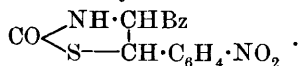
Thiocarbamide gives a deep yellow *product*, m. p. 176—177° (decomp.), to which the alternative formulæ,

$$\text{NH:C}{<}^{\text{NH·CHBz}}_{\text{S——CH·C}_6\text{H}_4\text{·NO}_2} \quad \text{or} \quad \text{NH:C}{<}^{\text{NH·CH·C}_6\text{H}_4\text{·NO}_2}_{\text{S——CHBz}},$$
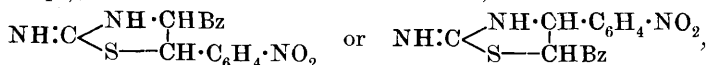
are assigned. Thiocarbanilide forms a yellow *product*, m. p. 221° (decomp.), which would be the diphenyl derivative of the foregoing substance. It gives unstable additive compounds with bromine

and iodine, and is converted by boiling with sodium ethoxide solution into an orange-red *isomeride*, m. p. 245°.   J. C. W.

Action of Light on Keto-oxido-compounds. SVEN BODFORSS (*Ber.*, 1918, **51**, 214—219).—Benzoylphenylethylene oxide, benzoyl-*m*-nitrophenylethylene oxide, and benzoyl-*p*-chlorophenylethylene oxide undergo rearrangement into phenyl α-hydroxystyryl ketones with increasing readiness when their methyl-alcoholic solutions are exposed to the light of a mercury lamp. The yields of the isomerides are very small, but their presence can be demonstrated by the ferric chloride test for enols and by the precipitation of copper salts, from which they can eventually be isolated.

The production of phenyl *m*-nitro-α-hydroxystyryl ketone by another method has already been described (A., 1917, i, 224). A third method consists in the action of *m*-nitrobenzoyl chloride on benzoylacetone in the presence of sodium ethoxide, followed by hydrolysis of the acetyl derivative by boiling hydrochloric acid. *Phenyl* p-*chloro-α-hydroxystyryl ketone*, $COPh \cdot CH\overset{:}{:}C(OH) \cdot C_6H_4Cl$, very pale yellow crystals, m. p. 89°, is also prepared as follows: *p*-chlorobenzylideneacetophenone is treated with bromine, when two isomeric *dibromides*, $COPh \cdot CHBr \cdot CHBr \cdot C_6H_4Cl$, are formed, a sparingly soluble one, m. p. 178—180°, decomp. 190—193°, and a freely soluble one, m. p. 125—126°, decomp. 142—143°, either of which gives the desired keto-enol on boiling with alcoholic potassium hydroxide.   J. C. W.

Action of Hydriodic Acid on Cinchonine and its Isomerides. Cinchoniline, Cinchonigine, and *apo*Cinchonine. E. LÉGER (*Compt. rend.*, 1918, **166**, 469—472. Compare this vol., i, 121).—When heated with hydriodic acid, cinchonine and cinchoniline give the same hydriodocinchonine, whilst cinchonigine and *apo*cinchonine give an isomeric *hydriodo*apo*cinchonine*, as shown by a study of the optical activity of the dihydrochlorides and dinitrates of the four hydriodo-derivatives.   W. G.

Preparation of Histidine. HARRY M. JONES (*J. Biol. Chem.*, 1918, **33**, 429—431).—Two litres of hydrochloric acid are added to an equal volume of the concentrated suspension of red blood corpuscles obtained by centrifugalising defibrinated ox blood. The mixture is boiled on a sand-bath for eighteen hours, or until the biuret reaction is negative. After exactly neutralising by the addition of about an equal volume of saturated sodium carbonate solution, the mixture is filtered, and ammonia removed from the filtrate by boiling for an hour with 25 grams or more of sodium hydroxide. On cooling, leucine and tyrosine are deposited, and should be filtered off. The histidine is now precipitated by the alternate addition of concentrated solutions of mercuric chloride and sodium carbonate until a filtered portion no longer gives a voluminous precipitate with the mercuric chloride solution. The precipitate is collected, washed, suspended in five times its volume

of water, and, using hydrochloric acid, the latter rendered acid to bromophenol-blue ($p_H = 3$). The mercury–histidine compound dissolves, and, after filtration, is reprecipitated by sodium carbonate. It is finally suspended in water and the histidine liberated by hydrogen sulphide. After filtration, the filtrate is concentrated at the ordinary temperature, whereon large, yellow crystals of histidine hydrochloride separate from the brown, syrupy mother liquor. The yield is about 15 grams.   H. W. B.

Conversion of Cocaine into New, Physiologically Active Substances. J. VON BRAUN and E. MÜLLER (*Ber.*, 1918, **51**, 235—252).—Von Braun has begun an inquiry into the interesting question of the influence on physiological activity of displacing some specific group or other from one position to another in the molecule of an active drug. So far, he has experimented on codeine (A., 1916, i, 665; 1917, i, 163), but this is not quite a suitable material, as its constitution is still not definitely known. The problem has now been attacked in the group of the tropeines, in which the presence of an acylated hydroxyl group in the γ-position with regard to the basic nitrogen atom may be regarded as the factor controlling the physiological behaviour. The question raised, therefore, in this paper is what is the effect of displacing the hydroxyl group to another part of the molecule, still in the γ-position with regard to the nitrogen atom? Cocaine (I) has been converted into two such compounds, II and III.

$$
\begin{array}{c}
CH_2 \cdot CH{-}CH \cdot CO_2Me \\
| \qquad\quad NMe \;\; CH \cdot OBz \\
CH_2 \cdot CH{-}CH_2 \\
(I.)
\end{array}
$$

$$
\begin{array}{cc}
CH_2 \cdot CH{-}CH \cdot CH_2 \cdot O \cdot CO & \quad CH_2 \cdot CH{-}CH \cdot CO_2Et \\
| \;\; NMe \;\; CH_2 \qquad CHPh & \quad | \;\; N{-}CH_2 \cdot CH_2 \cdot CH_2 \cdot OBz \\
CH_2 \cdot CH{-}CH_2 \qquad CH_2 \cdot OH & \quad CH_2 \cdot CH{-}CH_2 \cdot CH_2 \\
(II.) & (III.)
\end{array}
$$
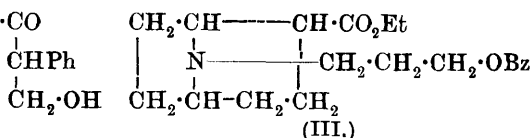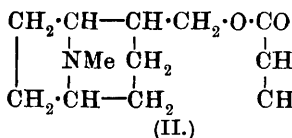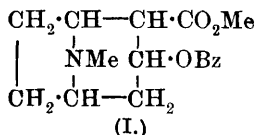
Compound II is actually found to be as effective a mydriatic as atropine, and III as powerful a local anæsthetic as cocaine. It follows, therefore, that it does not matter where the acyloxy-group is with regard to the tropane ring as long as it is in the γ-position with respect to the nitrogen atom.

Cocaine is converted by well-known methods into ecgonidine (formerly anhydroecgonine), and this into the ethyl ester (annexed formula). This is reduced by means of

$$
\begin{array}{c}
CH_2 \cdot CH{-}CH \cdot CO_2Et \\
| \;\; NMe \;\; CH \\
CH_2 \cdot CH{-}CH
\end{array}
$$

hydrogen and palladium to *ethyl dihydro-ecgonidine*, b. p. 127—129°/12 mm., which forms an *aurichloride*, yellow leaflets, m. p. 167°, and a *methiodide*, long needles, m. p. 219°. Willstätter (A., 1897, i, 385) reduced the ester by means of sodium and amyl alcohol; his pro-

duct had the same b. p., but gave quite different salts, and it is fairly obvious that transformation about the asymmetric carbon atom had occurred to a considerable extent in his experiment. The next stage consists in reducing the ester by means of sodium and alcohol to the hydramine, and Willstätter's product gives the same result as the above. The new base, *homotropine* (annexed formula), crystallises in needles, m. p.
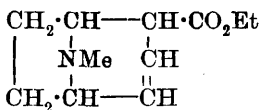
$$CH_2 \cdot CH \text{---} CH \cdot CH_2 \cdot OH$$
$$| \quad NMe \quad CH_2$$
$$| \quad\quad |$$
$$CH_2 \cdot CH \text{---} CH_2$$
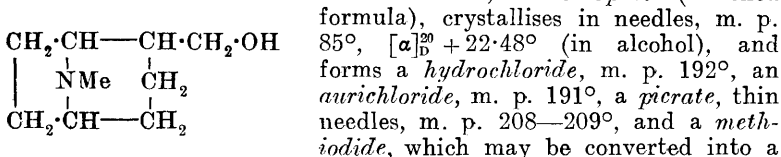
85°, $[a]_D^{20} + 22 \cdot 48°$ (in alcohol), and forms a *hydrochloride*, m. p. 192°, an *aurichloride*, m. p. 191°, a *picrate*, thin needles, m. p. 208—209°, and a *methiodide*, which may be converted into a *platinichloride*, m. p. 183°, and an *aurichloride*, yellow leaflets, m. p. 238°. The *benzoate* is produced by means of benzoyl chloride; it is a viscous oil, which forms a *platinichloride*, m. p. 201°, an *aurichloride*, m. p. 161°, and a lemon-yellow *picrate*, m. p. 177°. *Homotropine tropate* (II) is prepared by warming the hydrochloride with acetyltropyl chloride, hydrolysing the product by warm water to remove the acetyl group, and adding dilute sodium hydroxide to the solution; it is obtained as an oil, which forms a *platinichloride*, m. p. 192°. The oily *mandelate* and its *platinichloride*, m. p. 192°, are formed in the same way.

For the preparation of the other compound (III), cocaine is first treated with cyanogen bromide in warm chloroform, when *cyanonorcocaine* (IV), m. p. 123—124°, is produced. This is heated

$$CH_2 \cdot CH \text{-----} CH \cdot CO_2Me \qquad CH_2 \cdot CH \text{---} CH \cdot CO_2Et$$
$$| \quad N \cdot CN \quad CH \cdot OBz \qquad | \quad NH \quad CH$$
$$| \quad\quad\quad | \qquad\qquad | \quad\quad ||$$
$$CH_2 \cdot CH \text{-----} CH_2 \qquad\quad CH_2 \cdot CH \text{---} CH$$
$$\text{(IV.)} \qquad\qquad\qquad\qquad \text{(V.)}$$

with concentrated hydrochloric acid at 120°, and thus converted directly into *norecgonidine*, which is very sparingly soluble in alcohol, has m. p. 254—255°, forms a *hydrochloride*, m. p. 257°, a *platinichloride*, m. p. 251°, an *aurichloride*, m. p. 204°, and an *ethyl* ester (V), a basic-smelling oil, b. p. 157°/25 mm., which gives a very hygroscopic *hydrochloride*, long needles, an *aurichloride*, m. p. 133°, and a *benzoyl* derivative, m. p. 114°. Norecgonidine may also be prepared by first treating ethyl ecgonidine (above) with cyanogen bromide, but the yield is very small, rupture of the tropane ring being the main result. The ester V is hydrogenated in the presence of palladium, giving *ethyl dihydronorecgonidine*, b. p. 135—137°/19 mm., D_4^{19} 1·0856, $[a]_D^{19} + 5·881°$, which yields a hygroscopic *hydrochloride*, m. p. 149—150°, and an *aurichloride*, m. p. 110°. The N-γ-*benzoyloxypropyl* derivative (III) is prepared by the action of γ-bromopropyl benzoate (compare A., 1916, i, 631); it is an oil which forms a *hydrochloride*, long needles, m. p. 142°, a *platinichloride*, m. p. 94—95°, and an *aurichloride*, m. p. 127—128°.

Another interesting product is obtained by the action of γ-bromopropyl benzoate on the ester V. It is designated *eccaine*, and is

an oil which forms a *hydrochloride*, m. p. 117°, a *picrate*, m. p. 139—141°, and a *methiodide*, m. p. 194—195°. It is more active as an anæsthetic than cocaine, is non-toxic, and so stable that its solutions may be sterilised easily.　　　　　　J. C. W.

Preparation of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 296742; from *Chem. Zentr.*, 1917, i, 612).—Compare preceding abstract.　　　　　　J. C. W.

Preparation of *N*-Demethylated Derivatives of the Alkaloids of the Cocaine and Atropine Groups, their Derivatives and Salts. CHEMISCHE WERKE, GRENZACH (D.R.-P., 301870; from *Chem. Zentr.*, 1918, i, 250).—Compare von Braun and Müller (above). Acetyltropine reacts with cyanogen bromide to give *acetylcyanonortropine*, m. p. 96°, which yields nortropine on boiling with moderately concentrated hydrochloric acid.
　　　　　　J. C. W.

Production of Derivatives of Homotropine. CHEMISCHE WERKE, GRENZACH (D.R.-P., 299806; from *Chem. Zentr.*, 1917, ii, 510).—The pharmacologically inactive homotropine can be rendered active by esterification with organic acids such as benzoic, tropic, or mandelic acid, the resulting esters (see von Braun and Muller, preceding page) resembling atropine in their effect on the animal organism. In this way, anhydroecgonine, hitherto value-less, can be converted into therapeutically useful products.
　　　　　　D. F. T.

New Cases of Isomerism in the Isatin Series. GUSTAV HELLER [with FRITZ BAUMGARTEN] (*Ber.*, 1918, **51**, 180—190. Compare A., 1917, i, 219).—The discovery of three different forms of isatin, or at least ethers of three forms, has led the author to examine 5:7-dimethylisatin, with the surprising and so far in-explicable result that no fewer than four individual isomerides have been obtained. These are numbered I, II, III, and IV, for the time being, in the order of their discovery.

Isomeride I.—This is the normal product, $C_6H_2Me_2{<}^{CO}_{NH}{>}CO$, obtained originally from dichloroacetic acid and 1:3:4-xylidine (A., 1908, i, 218). It crystallises in yellow needles, m. p. 243°, and forms a greyish-red N-*silver* salt, from which 1:5:7-*trimethylisatin* may be obtained, in dark red leaflets, m. p. 214°, this yielding a yellow *phenylhydrazone*, m. p. 161°. The sodium salt of the isatin reacts with silver nitrate to form a very dark brown O-*silver* salt, $C_6H_2Me_2{<}^{CO}_{N}{>}C{\cdot}OAg$, but this yields the original isatin on acidification or treatment with methyl iodide, and not the lactim modification or its methyl ether.

Isomeride II.—This is produced by the action of benzoyl chloride on the above *N*-silver salt, suspended in warm benzene. It crystallises in large, dark red, oblique prisms, m. p. 204° (decomp.); it gives the indophenin reaction at once, whereas the colour only develops slowly with isomeride I; it dissolves in pure sulphuric acid with dark violet colour, whereas isomeride I gives a ruby-red solution; it is insoluble in sodium hydroxide solution; it forms a *phenylhydrazone*, which is fairly soluble in alcohol and crystallises in yellow needles, m. p. 216° (decomp.), whereas the phenylhydrazone of isomeride I is very sparingly soluble and has m. p. 272°; and it reacts with methyl sulphate, which isomeride I does not, giving a *methyl ether*, quadratic, red tablets, m. p. 247° (decomp.), which forms a yellowish-red *phenylhydrazone*, m. p. 203°. These reactions serve to establish the fact that the second isomeride is a distinct individual, but that it is neither the lactim modification nor the expected isatol, that is, neither

$$C_6H_2Me_2\!\!<^{CO}_{-N}\!\!>C\cdot OH \quad \text{nor} \quad C_6H_2Me_2\!\!<^{C(OH)}_{N----}\!\!>CO.$$
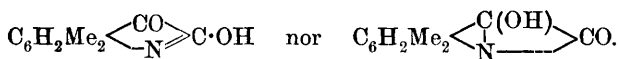
Isomeride III.—This is formed by triturating isomeride II with dilute sodium hydroxide, when a red, sparingly soluble sodium salt is produced, which is acidified. It crystallises in bluish-red, rectangular prisms, m. p. 279°; it yields the same sodium salt when mixed with sodium hydroxide, but if the suspension is kept, the colour fades and the isomeride I may be recovered on acidifying; it is freely soluble in dilute sodium carbonate or ammonia; it does not give the indophenin reaction, and its solution in concentrated sulphuric acid is only faintly reddish-yellow; it does not give a phenylhydrazone; it forms a bluish-red *silver* salt; and it may be converted, through the sodium or silver salts, or by means of diazomethane, into a *methyl ether*, yellowish-red tablets, m. p. 210°, insoluble in warm, dilute alkali hydroxides. This modification therefore conforms to the type of isatol.

Isomeride IV.—This is produced when isomeride III is crystallised from hot acetic acid. It has m. p. 267°, forms a readily hydrolysable, colourless sulphate, dissolves in alcoholic potassium hydroxide, does not yield a phenylhydrazone, and reacts with diazomethane to form a *methyl ether*, fiery-red, glistening, flat prisms, m. p. 211°, which depresses the m. p. of the methyl derivative of isomeride III. The compound is therefore another isatol.

There are, apparently, two pairs of structurally similar isomerides, I and II being of the normal isatin type and III and IV of the isatol series, but I and III resemble each other in their acidic properties and II and IV in their neutral or basic properties.

<div align="right">J. C. W.</div>

Bz-**Hydroxyindolinones** [**Hydroxyoxindoles**]. GEORG WAHL (*Monatsh.*, 1918, **38**, 525—535).—No oxindole has hitherto been prepared containing a hydroxyl group in the benzene nucleus. By extending the indolinone synthesis, based on the

elimination of ammonia from aliphatic phenylhydrazides (Brunner, A., 1897, i, 100), to the corresponding anisylhydrazides, it is possible to obtain 5-methoxyoxindole derivatives. Thus, iso*butyryl* p-*anisylhydrazide*, colourless leaflets or granules, m. p. 142°, when heated with lime at approximately 180° for about two hours, yields 5-*methoxy*-3 : 3-*dimethyloxindole*, $\begin{matrix} CMe_2\text{---}CO \\ C_6H_3(OMe) \end{matrix}\!\!>\!\!NH$, rhombic tablets, m. p. 150° (*bromo*-derivative $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 218°; *acetyl* derivative, needles, m. p. 84°; *benzoyl* derivative, needles, m. p. 82°; *silver* salt, very unstable, greenish-white, gelatinous mass), accompanied by a little *iso*butyrylamide, leaflets, m. p. 124°. By treating with boiling hydriodic acid for one hour, the methoxyl compound is converted into 5-*hydr-oxy*-3 : 3-*dimethyloxindole*, $\begin{matrix} CMe_2\text{---}CO \\ C_6H_3(OH) \end{matrix}\!\!>\!\!NH$, colourless needles, m. p. 244°; *diacetyl* derivative, colourless needles, m. p. 126°; *benzoyl* derivative, $C_{17}H_{15}O_3N$, needles, m. p. 240°. In a similar manner, iso*butyryl* o-*anisylhydrazide*, m. p. 120°, when heated with lime, is converted into 7-*methoxy*-3 : 3-*dimethyloxindole*, $C_{11}H_{13}O_2N$, colourless needles, m. p. 101° (*bromo*-derivative, $C_{11}H_{12}O_2NBr$, colourless needles, m. p. 200°), which is demethylated by hydriodic acid with formation of 7-*hydroxy*-3 : 3-*dimethyloxindole*, $C_{10}H_{11}O_2N$, m. p. 250°. D. F. T.

Selenomethylene-blue. P. KARRER (*Ber.*, 1918, **51**, 190—192). —In his account of some new selenazine dyes, the author showed that the true selenium analogue of methylene-blue had not yet been described, references to such a dye being erroneous (A., 1916, i, 434). The compound is easily prepared by Kehrmann's method (*ibid.*, 435). Selenodiphenylamine is treated with bromine in glacial acetic acid until phenazselenonium perbromide is completely precipitated, in brightly shimmering, brown flakes, and this is triturated with an alcoholic solution of dimethylamine. 3 : 6-*Tetramethyldiaminophenazselenonium bromide* (*selenomethylene-blue bromide*), $NMe_2\cdot C_6H_3\!\!\ll\!\!\begin{matrix} N\text{---} \\ SeBr \end{matrix}\!\!>\!\!C_6H_3\cdot NMe_2$, is formed, and, after crystallisation from boiling water, is obtained in shimmering needles with metallic green reflex, possessing the same stability and tinctorial properties as methylene-blue. J. C. W.

Action of Aniline on Carbon Tetrachloride. ERNST JOHANNES HARTUNG (T., 1918, **113**, 163—168).—In 1858, Hofmann showed that carbon tetrachloride and aniline react at 180° to form pararosaniline and diphenylaminobenzamidine,
$$NHPh\cdot C(NPh)\cdot C_6H_4\cdot NH_2.$$
This reaction has now been studied at lower temperatures and in the presence of a copper–mercury couple as a catalyst.
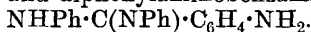
The two liquids react even at the ordinary temperature. Brown discolorations soon appear, but the first definite product, after

some weeks' action, seems to be s-diphenylcarbamide. The production of this can be traced to the action of moisture on a dichloro-compound, $CCl_2(NHPh)_2$. After some months, diphenylaminobenzamidine separates. The by-products vary according to the proportions of the reagents employed. With a very large excess of carbon tetrachloride, a compound which crystallises in small, reddish-brown prisms, m. p. 245° (corr.), and a dark blue dye separate, as well as diphenylcarbamide, during the early months.

In the presence of amalgamated copper, the mixtures solidify within a few days, diphenylaminobenzamidine hydrochloride being the chief product, accompanied by azobenzene, phenylcarbylamine, and a little pararosaniline. The reaction is still more rapid at 80—90°, but is never complete, and many obscure by-products are formed.

Diphenylaminobenzamidine hydrochloride becomes yellow on rubbing, but reverts to white after some days. These changes can be induced repeatedly.   J. C. W.

Reactions of the Formamidines. VII. The Constitution of some Pyrazole Derivatives. F. B. DAINS and ROLLA N. HAEGER (*J. Amer. Chem. Soc.*, 1918, **40**, 562—569. Compare A., 1902, i, 602; 1906, i, 781; 1913, i, 1086, 1096; 1916, i, 676).—It has already been shown that the substituted formamidines react with compounds containing methylene hydrogen, giving rise to products in which the –CH$_2$– group is replaced by the grouping :CH·NHR. By the action of hydrazine on amino-methylene derivatives of ethyl acetoacetate, it is now found that derivatives of 5-methylpyrazole-4-carboxylic acid can be obtained.

m-*Bromoanilinomethyleneacetoacetanilide*,
$$NHPh·CO·CAc\dot{:}CH·NH·C_6H_4Br,$$
yellowish-white needles, m. p. 113°, prepared by the interaction of *m*-dibromodiphenylformamidine and acetoacetanilide or aceto-*p*-toluidide, reacts with hydrazine in alcoholic solution, yielding *5-methylpyrazole-4-carboxyanilide*, $\begin{array}{c}N\underline{=\!\!=}CH\\NH·CMe\end{array}\!\!>C·CO·NHPh,$
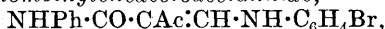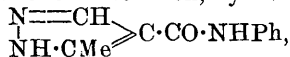
needles, m. p. 179°, the same substance also being obtained by the action of hydrazine on anilinomethyleneaceto-*p*-toluidide, the reaction product of acetoaceto-*p*-toluidide and diphenylformamidine. When heated together at 120—130°, ethyl acetoacetate and *o*-phenetidine undergo condensation, with formation of *acetoaceto-o-phenetidide*, $CH_2Ac·CO·NH·C_6H_4·OEt$, needles, m. p. 92°, which is capable of reacting with diphenylformamidine, with formation of *anilinomethyleneacetoaceto-o-phenetidide*,
$$NHPh·CH\dot{:}CAc·CO·NH·C_6H_4·OEt,$$
needles, m. p. 135°; hydrazine or hydrazine hydrate converts this into *5-methylpyrazole-4-carboxy-o-phenetidide*,
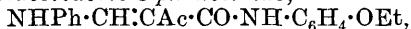
$$\begin{array}{c}N\underline{=\!\!=}CH\\NH·CMe\end{array}\!\!>C·CO·NH·C_6H_4·OEt,$$
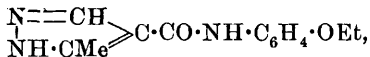
needles, m. p. 163°; *hydrochloride*, m. p. 200° (decomp.).   At

100°, ethyl acetoacetate reacts with di-o-phenetidylformamidine, giving *ethyl* o-*phenetidinomethyleneacetoacetate*, $C_{15}H_{19}O_4N$, colourless crystals, m. p. 111°, which on treatment in hot alcoholic solution with hydrazine hydrate yields *ethyl* 5-*methylpyrazole*-4-*carboxylate*, $\underset{\text{NH·CMe}}{\overset{\text{N}=\!=\!\text{CH}}{\big|}}{>}\!\text{C·CO}_2\text{Et}$, needles with $1H_2O$, m. p. 46°, or m. p. 54° when anhydrous.

Phenylhydrazine reacts with anilinomethyleneacetylacetone, giving rise to 4-acetyl-1-phenyl-5-methylpyrazole, in agreement with Claisen's results (A., 1897, i, 441), but with ψ-cumidinomethyleneacetylacetone and p-toluidinomethyleneacetylacetone, this product is accompanied by the *phenylhydrazone*, yellow needles, m. p. 175°, of the acetylphenylmethylpyrazole. The reaction product of acetylphenylmethylpyrazole and hydrazine hydrate in alcoholic solution is the corresponding *hydrazone*, $\underset{\text{NPh·CMe}}{\overset{\text{N}=\!=\!\text{CH}}{\big|}}{>}\!\text{C·CMe:N·NH}_2$, foursided prisms, m. p. 94·5° (*hydrochloride*, m. p. 218°; *benzylidene* derivative, $C_{10}H_9N_2\text{·CMe:N·N:CHPh}$, yellow crystals, m. p. 127°), which when warmed with a little formic or acetic acid in ethyl acetate solution undergoes intermolecular condensation, with formation of hydrazine and *bis*-4-*acetyl*-1-*phenyl*-5-*methylpyrazolylazine*, $N_2(\text{:CMe·}C_{10}H_9N_2)_2$, yellow crystals, m. p. 174°; this, on boiling with hydrochloric acid, regenerates the original pyrazole compound. When o-phenetidinomethyleneacetylacetone and hydrazine hydrate are warmed together in alcoholic solution, a yellow compound, m. p. 320°, is obtained; this has already been described by Gaugler and by J. Gattermann (*Diss.*, Freiburg, 1903 and 1904), who regarded it as the triazine, $\underset{\text{CH}_2\text{·C:N}—\text{NH}}{\overset{\text{CH}=\text{C·CMe:N}}{\big|\qquad\big|\qquad\big|}}$, but a more probable constitution is that of the azine derivative of 4-acetyl-5-methylpyrazole.

During the course of the investigation, *acetoaceto*-m-*bromoanilide*, $CH_2Ac\text{·CO·NH·}C_6H_4Br$, plates, m. p. 83°, and m-*bromoanilinomethyleneacetoaceto*-m-*bromoanilide*,

$$C_6H_4Br\text{·NH·CO·CAc:CH·NH·}C_6H_4Br,$$
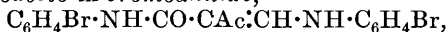
pale yellow needles, m. p. 154°, were prepared, the latter by the interaction of ethyl acetoacetate and di-m-bromodiphenylformamidine. It was also found that the benzoyl derivative of m-bromoaniline has m. p. 135—136° instead of 120°, as stated earlier (Kottenhahn, A., 1891, 1237). The results of the investigation demonstrate that the reaction products of hydrazine or phenylhydrazine and arylaminomethyleneacetoacetoarylamides are pyrazole compounds, and not pyrazolone derivatives, as has been assumed earlier (Ruggeburg, *Diss.*, Freiburg, 1903; J. Gattermann, *Diss.*, 1904). D. F. T.

Preparation of Mono-azo-dyes suitable for the Manufacture of Pigments. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 297414; from *Chem. Zentr.*, 1917, i, 981—982).—In place of 1-benzoylamino-7-hydroxynaphthalene, or derivatives of

this containing substituents in the benzoyl radicle, the corresponding *N*-alkyl compounds can be used. 1-Benzoylethylamino-7-hydroxynaphthalene, 1-benzoylmethylamino-7-hydroxynaphthalene, and 1 : 2′-chlorobenzoylethylamino-7-hydroxynaphthalene have m. p. 224—225°, 186—187°, and 232—233° respectively.

<div align="right">D. F. T.</div>

Structure of Yeast-nucleic Acid. III. Ammonia Hydrolysis. P. A. LEVENE (*J. Biol. Chem.*, 1918, **33**, 425—428. Compare this vol., i, 130).—Uridinephosphoric acid can be isolated from the products of the hydrolysis of yeast-nucleic acid by dilute ammonia at 115° through the intermediate formation of the mixed brucine salts of the cytosine and uracil nucleotides, which, after separation, are converted into the barium salts, as previously described (*loc. cit.*). H. W. B.

Effects of Electrolytes on Gelatin and their Biological Significance. II. Effect of Salts on the Precipitation of Acid and Alkali-gelatin by Alcohol. Antagonism. W. O. FENN (*J. Biol. Chem.*, 1918, **33**, 439—451. Compare this vol., i, 198).—Employing the technique previously described, the author finds that the effect of combinations of salts with acids and alkalis on the precipitability of the gelatin by alcohol is greater or less than the effect produced by the acid or alkali alone, according to the valency of the ions in the salt. Thus, salts with univalent ions (like sodium chloride) decrease the effect of both acids and alkalis on the precipitability of gelatin. Salts with bivalent or tervalent ions (like calcium or aluminium chloride) decrease the effect of alkalis on gelatin, but increase the effect of acid, except in high concentrations of salt or acid, where the effect is decreased. Salts with bivalent or tervalent anions (like sodium sulphate or citrate) decrease the effect of acids on gelatin, but increase the effect of alkalis, except at high concentration, when the greater the concentration of either salt or alkali, the less the alcohol necessary for precipitation. These results are comparable and in some respects analogous to the antagonistic effects of various electrolytes observed in certain biological phenomena (compare Loeb, A., 1916, i, 186, and this vol., i, 51). H. W. B.

Ionisation of Proteins and Antagonistic Salt Action. JACQUES LOEB (*J. Biol. Chem.*, 1918, **33**, 531—549. Compare A., 1917, ii, 453, and Fenn, preceding abstract).—The author describes a new method of studying the effect of neutral salts on gelatin in which the powdered protein is treated with the salt in a concentration of $M/4$ or $M/8$, and then the excess of salt is removed by washing with water or with a weak solution of another salt. In these circumstances, the initial swelling occurring in $M/8$-sodium chloride is greatly increased by perfusion with water or a weak solution of a neutral salt with a univalent metal. The additional swelling is only possible as long as the weaker solution remains below a certain concentration, and it is found that the limiting

molecular concentration which will cause the additional swelling is twice as great if the anion is univalent as when it is bivalent, regardless of the nature of the anion and cation. The influence of neutral salts on the swelling of gelatin is therefore of a stoicheiometric order, and the inhibiting action of a salt on the additional swelling is explained by the author as being due to a diminution of the degree of electrolytic dissociation of a metal–protein compound first produced. Thus, neutral salts with a univalent cation like sodium chloride in concentrations of $M/8$ or $M/4$ form highly ionisable salts with gelatin. On treatment with water, dissociation occurs into positively charged metal ions and negative gelatin ions, which may or may not contain the anion of the salt in non-dissociated bondage. It is the formation of these gelatin ions that causes the additional swelling observed. The metals of the alkaline earth group form salts with gelatin which are not capable of swelling and do not ionise. The transformation of gelatin salts with univalent cation (capable of swelling) into gelatin salts with bivalent cation (not capable of swelling) is the cause of the antagonistic action of the metals of the calcium group.

H. W. B

Physiological Chemistry.

The Presence of Hæmatin in Human Blood-serum. I.
JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **85**, 171—187).—As a result, chiefly of clinical experience, hæmatin could be detected as a pathological constituent of the blood after intoxication by the following substances: chromates, chlorates, carbon monoxide, various gases, resorcinol, mono-, di-, and tri-nitrobenzene, picric acid, acetanilide, exalgin, *p*-phenylenediamine, pyrodine (acetylphenylhydrazine), maretine, trional, trigemine, excessive use of tobacco.

S. B. S.

The Presence of Hæmatin in Human Blood-serum. II.
JOH. FEIGL and RUD. DEUSSING (*Biochem. Zeitsch.*, 1918, **85**, 212—229).—This paper is chiefly of clinical interest, giving the results of the examination of the serum for the presence of hæmatin in about 700 cases.

S. B. S.

Chemical Studies on Physiology and Pathology. II. Immunity Reactions. G. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **85**, 1—44. Compare this vol., i, 47).—A theoretical paper, in which the authors develop further their conceptions of the nature of proteins, which have been already the subject of numerous papers. They conceive the antibodies as derived from the antigen itself; this undergoes a partial degradation in the body, and the degraded but still specific product is then adsorbed by certain protein particles of the blood (derived from the degrada-

tion of cells and in the "globulin" stage). The complex thus formed has the property of adsorbing new quantities of antigen, thus giving rise to the known immunity reactions, such as precipitation, deintoxication, etc. The ideas thus expressed are developed in considerable detail.   S. B. S.

Deaminisation and Carbamide Formation in the Animal Body. WILHELM LÖFFLER (*Biochem. Zeitsch.*, 1918, **85**, 230—294). —The surviving liver (rabbits and dogs) was perfused with Ringer's solution mixed with blood, and the ammonia and carbamide were estimated in the perfusing fluid both before and after perfusion. The carbamide was estimated by the urease method. It is shown that there is an increase in the carbamide after perfusion even when no nitrogen compound is added to the perfusion liquid. The addition of the ammonium salts of inorganic acids causes, however, a considerable addition to the amount of carbamide formed, leaving no doubt that the ammonium salts are converted into carbamide, and this happens even when the perfusing liquid is distinctly acid. Acids inhibit the formation of carbamide somewhat, without preventing it. Primary amines give rise to carbamide also when perfused through the liver, the lower amines, such as methylamine or ethylamine, being completely burnt, and the higher amines (amylamine, benzylamine, *p*-hydroxyaniline, and phenylethylamine) less completely. No substituted carbamides could be detected. Trimethylamine is completely demethylated in the liver, the ammonia being converted into carbamide.   S. B. S.

Presence of the Co-ferment of the Alcoholic Yeast Fermentation in Muscular Tissue and its Significance in the Respiratory Mechanism. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **101**, 165—175).—The extracts of muscle and other tissues are prepared by boiling the minced tissue in an equal weight of water and filtering. Samples of yeast juice which have been inactivated by removal of the co-ferment by Harden and Young's method (A., 1907, i, 104) are reactivated by the addition of the tissue extract. The author finds that glycolysis by yeast or by muscle juice is similarly accelerated by the tissue extract (compare Harden and MacLean, A., 1911, ii, 215, 905).   H. W. B.

The Synthesis of Luciferin. RAPHAEL DUBOIS (*Compt. rend.*, 1918, **166**, 578—580. Compare *ibid.*, 1917, **165**, 33, and Harvey, A., 1917, i, 365).—The author has extracted from *Pholade dactyle* a substance presenting all the characteristics of taurine, and also a luciferase which converts the taurine into luciferin.   W. G.

[Physiological] Action of an Isomeride of Caffeine. WILLIAM SALANT and HELENE CONNET (*J. Pharm. Exper. Ther.*, 1918, **11**, 81—88).—The authors find that 2:8-dioxy-1:7:9-trimethyl-1:2:8:9-tetrahydropurine (Johns, A., 1914, ii, 922) is

much less active physiologically than the isomeric 2:6-dioxy-compound (caffeine), the relative toxicity for rabbits of the two substances being about 1:11. The new isomeride caused a moderate increase in the secretion of urine in some experiments, but it failed to stimulate renal activity in others. When tested on frogs, it was found to act as a weak cardiac stimulant.   H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Disinfectant Action of Quinine Alkaloids on Pathogenic Bacteria. R. BIELING (*Biochem. Zeitsch.*, 1918, **85,** 188—211. Compare Schaeffer, this vol., i, 93).—The alkaloids investigated were quinine, optochine (ethylhydrocupreine), eucupine (*iso*amyl-hydrocupreine), and the *iso*octyl-, decyl-, and dodecyl-hydro-cupreines. These have been found to have a specific disinfectant action on the bacilli of diphtheria, splenic fever, and tetanus. Eucupine and *iso*octylhydrocupreine are generally the most effective.   S. B. S.

Influence of Acids on Germination. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1918, **166,** 547—552).—Mineral acids must be classed amongst those substances considered most injurious to germination. This toxic action may be modified by the presence of electrolytes in the form of salts, or by those that the acid may form by its action on the teguments of the seeds or the glass of the apparatus. Amongst these antitoxic substances, calcium appears to be one of the most powerful.   W. G.

The Assimilation of Carbon Dioxide. III. Behaviour of Colloidal Chlorophyll towards Carbon Dioxide. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Ber.*, 1917, **50,** 1791—1801. Compare this vol., i, 207).—Solutions of chlorophyll in organic solvents do not absorb more carbon dioxide than the pure liquids, but the hydrosols absorb much more of the gas than other colloidal solutions, the absorption reaching a maximum of two molecular proportions to every magnesium atom. The absorption is attended by the precipitation of phæophytin, and the reaction may consequently be represented, in the case of chlorophyll-*a*, by the equation $C_{55}H_{72}O_5N_4Mg + 2CO_2 + 2H_2O = C_{55}H_{74}O_5N_4 + Mg(HCO_3)_2$. Carbon dioxide has therefore the power of breaking the two links between the metal and nitrogen atoms in the molecule.

Before the magnesium is completely removed, however, an important intermediate compound, of the nature of a hydrogen carbonate, is formed. As this has the same colour as chlorophyll,

the subsidiary valency chromophoric complex is still existent, thus:

$$\equiv N\cdot C\vdots C\cdot C\cdot N\cdot C- \qquad\qquad \equiv N\cdot C\vdots C\cdot C\cdot NH\cdot C-$$
$$>Mg \quad + CO_2 + H_2O \rightleftharpoons \quad >Mg\cdot O\cdot CO_2H$$
$$\equiv N\cdot C\vdots C\cdot C\cdot N\cdot C- \qquad\qquad \equiv N\cdot C\vdots C\cdot C\cdot N\cdot C-$$
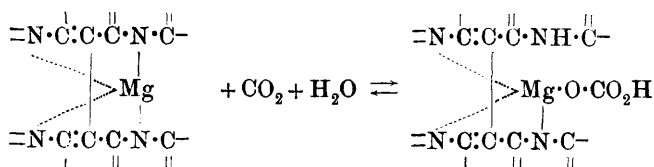
The evidence in favour of the existence of such an intermediate compound is as follows. (1) If a chlorophyll hydrosol is partly saturated with carbon dioxide, then extracted with ether, and the ash of the pigment is estimated, it will be found that the magnesium content is greater than it would be if the gas had directly eliminated the metal. (2) If partly saturated solutions are poured into alcohol (4 parts) and purified air is bubbled through the solution, all the carbon dioxide is recovered and chlorophyll is reproduced.

If the partly saturated hydrosols themselves are allowed to dissociate, however, the carbon dioxide is not quantitatively recovered. Hydrolysis takes place, which in the case of chlorophyll-a results in the quantitative formation of phæophytin and the basic carbonate, $4MgCO_3,Mg(OH)_2$. With chlorophyll-b, a certain amount of chlorophyll is regenerated.

The obvious suggestion is, therefore, that chlorophyll in the leaf unites with carbon dioxide in a similar way, but the conditions are not quite the same. The speed at which carbon dioxide is absorbed by the leaf is much greater than it is in the case of the hydrosol, and the leaf thrives in an atmosphere containing as much as 20% of carbon dioxide, which is a concentration that would very soon lead to the decomposition of chlorophyll in solution. At any rate, the photosynthesis which goes on in the leaf is now to be regarded as an action of the light on the compound of carbon dioxide and chlorophyll, which consists in transforming the carbonic acid into a peroxidic isomeride, capable of parting with oxygen in the gaseous form. Two isomerides are possible, namely, per-formic acid, $H\cdot CO\cdot O\cdot OH$, which is known to change easily into carbonic acid (d'Ans and Frey, A., 1912, i, 601), and a hypothetical peroxide of formaldehyde, $OH\cdot CH\diagdown^O_O$ The latter possibility is discussed in the light of the fact that formaldehyde is the primary product in the photosynthesis of carbohydrates.

J. C. W.

The Permeability of Living Protoplasm to some Salts. ARTHUR TROENDLE (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 38—54, 117—132).—Salts in hypertonic solutions are absorbed at first with a constant velocity, characteristic for each salt, but after a certain quantity of the salt has been absorbed, the velocity of entry diminishes steadily. In the first stage there is a definite

ratio between the concentration and the time, and in the second stage there is a ratio between the concentration and the logarithm of the time. The entry of salts through living protoplasm does not obey Fick's law of diffusion. The nature of the cation controls the velocity of entry of a salt much more than that of the anion. In a group of chemical elements there is a concordance between the influence of an ion on the velocity of absorption and its position in the periodic classification of the elements. As an explanation of the experimental facts, the author suggests the following hypothesis. The salts irritate the protoplasm, which replies by transferring some of the salt to its interior. During this process, changes of an unknown character, designated by the term "fatigue," take place in the protoplasm. This fatigue, in increasing, obeys Weber's law.   W. G.

Soluble Carbohydrates in Green Leaves. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1918, **101**, 77—88).—The author estimates the amounts of various soluble carbohydrates in the leaves of plants collected at a period when the products of assimilation are at a maximum. *Tulipa sylvestris* and *Narcissus poeticus* contain 1% of sucrose in the fresh leaf, together with dextrose and other soluble sugars, but no starch. There is no sucrose or starch in *Gentiana brevidens*, the place of the latter being taken by an apparently new saccharide which reduces Fehling's solution, possesses a lævorotation, and on hydrolysis yields only dextrose. It is present to the extent of 2·5%, calculated on the fresh leaves. *Hemerocallis fulva*, *Fritilaria imperialis*, *Allium victoriale*, and *Veratrum nigrum* contain from 2 to 3% of carbohydrates soluble in water, whilst *Scilla sibirica* and *Iris germanica* contain from 1—2%. There are only traces of starch and reducing sugars in *Convallaria majalis*, but a considerable quantity of a polysaccharide of the inulin type, yielding lævulose on hydrolysis with acetic acid. Of the plants in the leaves of which starch is present, *Hosta Sieboldiana* and *Tilia europœa*, containing moderate amounts of starch, also contain 1—2% of soluble carbohydrates, whereas in *Taraxacum officinale*, *Bunias orientalis*, and *Acer platanoides*, containing much starch, there are only traces of saccharides soluble in water. With the exception of *Convallaria*, the amount of starch in the leaves is roughly inversely proportional to the amount of soluble carbohydrates present.   H. W. B.

Chemical Composition of "Assimilation-secretion" in Plants. ARTHUR MEYER (*Ber. Deut. bot. Ges.*, 1918, **35**, 674—680). —Previous investigations have shown that the globules (assimilation-secretion) occurring in chloroplasts may be differentiated from fat by microchemical means. They do not become crystalline on treatment with potassium hydroxide solution, and with strong nitric acid they exhibit pitting of the surface. They are soluble in alcohol, ether, or strong acetic acid, are turned brown by osmic acid, and reduce ammoniacal silver nitrate solution.

The total volume of the "secretion" in 1 kilo. of dark green

leaves of *Tropaeolum majus* is calculated to be approximately 0·5 c.c., and in old leaves of the same plant immediately prior to withering to be 2·14 c.c. The dried and powdered leaves of *Funkia Sieboldiana* on being heated at 120° gave a turbid distillate which possessed a characteristic odour and reduced ammoniacal silver nitrate solution.

The author assumes that the "assimilation-secretion" contains compounds related to the leaf-aldehyde isolated by Curtius and Franzen (compare A., 1912, ii, 797, 978, 979; 1914, i, 646), but it is also supposed that the "secretion" contains other constituents, since the amount of Δ^α-hexenaldehyde obtained by these investigators is much less than the total volume of the secretion observed by the author.   H. B. H.

The Manganese Content of the Ash of certain Drugs. L. E. WESTMAN and R. M. ROWAT (*J. Amer. Chem. Soc.*, 1918, **40**, 558—562).—Manganese appears to be fairly widely distributed in the vegetable kingdom (compare Hafner and Krist, *Zeitsch. Oesterr. Apoth. Ver.*, 1907, **45**, 387; Pichard, A., 1899, ii, 40; Jadin and Astruc, A., 1913, i, 948; McHargue, A., 1915, i, 48; Headden, *J. Agric. Res.*, 1915, **5**, 349). The manganese content of certain laxative drugs and allied species of plants, for example, *Rhamnus frangula* (alder buckthorn bark), *Cinnamomum cassia cortex* (cassia bark), *Rhamnus purshiana* (cascara sagrada), podophyllin root, senna leaves, rhubarb root, *Rhamnus californica* bark, licorice root, jalap root, *Euonymus atropurpureus* (wahoo bark), cassia pulp, and Barbadoes aloes has been examined; the first two exhibit a higher content of manganese than any similar plant tissue hitherto examined; the figures are somewhat variable, the maximum being 0·067%. In *Rhamnus purshiana*, it is found that the proportion of manganese in the inner third of the bark is about twice as great as in the outer third. When the powdered drugs of the Rhamnaceæ family are extracted with water, approximately one-fourth of the manganese goes into solution.   D. F. T.

The Degradation of Inulin and of the "Inulides" in Chicory Root. B. GESLIN and J. WOLFF (*Compt. rend.*, 1918, **166**, 428—430. Compare A., 1917, i, 720).—Chicory roots gathered in October or December and stored one month show a change in their inulin and inulide content. A portion of the inulin is converted into inulide, and some of the less readily fermented inulides undergo further degradation and are converted into the more readily fermented inulides.   W. G.

Occurrence of Catechol and Quinol. EDMUND O. VON LIPPMANN (*Ber.*, 1918, **51**, 272).—During the long spell of dry weather at the end of the summer of 1917, the author found deposits of almost pure catechol on the inner surfaces of the bark cast early in the morning by some old plane trees, and quinol

adhering in dense rings to the viscous exudations at the wounds caused by grafting some pear-trees.   J. C. W.

Microchemistry of Plants. VIII. Organic Crystalline Substances in Gentiana germanica. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1917, **35**, 653—657).—The occurrence of two distinct crystalline substances in the leaves of *Gentiana germanica* is recorded. The first of these is obtained as a sublimate of yellow, needle-like crystals when the dry leaves are subjected to micro-sublimation at moderate temperatures. This compound, to which the name *gentiolutein* is given, is insoluble in water, alcohol, glycerol, aqueous chloral hydrate, olive oil, or in 10% solutions of hydrochloric, sulphuric, or acetic acid, but is easily soluble in acetone. In barium and calcium hydroxide solutions, the crystals become deep brown and also give a transitory, bright bluish-green colour with calcium chloride solutions. Gentiolutein occurs not only in the leaves, but also in the stems and flowers of the above species, but could not be detected in *G. asclepiadea*, *G. ciliata*, or *G. pneumonanthe*, although *G. ciliata* yielded a colourless, crystalline substance, which, however, differed from gentiolutein in its relations to the various solvents. A second crystalline substance may be observed when, after removal of the epidermis, the leaf is immersed in distilled water, or when it is treated with 10% solutions of hydrochloric, sulphuric, or nitric acid, or with phenol, alcohol, or glycerol.

Evidence is adduced to show that neither of the substances observed is identical with gentiopicrin or gentianin; further chemical investigations are required.   H. B. H.

Conversion of Quicklime in Soil. G. HAGER (*J. Landw.*, 1917, **65**, 245—311).—Evidence confirmatory of earlier observations is given to show that when an application of quicklime is made to the soil, only a small proportion of the lime reappears as calcium carbonate. The remainder is adsorbed by the soil constituents, and it is impossible to detect the presence of free calcium hydroxide after even a very short period of digestion. This adsorption of lime may be due to surface action or to chemical causes, and is regarded as being associated with the observed increased adsorptive power of a soil for other bases, such as potash and ammonia, which results from an application of lime.

The power of a soil for adsorption appears to be related to its content of clay and the presence of unsaturated compounds, and under normal conditions an equilibrium between the absorptive and adsorptive power of the soil carbon dioxide and the soil compounds respectively is soon reached. The action of calcium carbonate is stated to be less rapid than that of calcium oxide, and some months may elapse before an equilibrium is obtained. The influence of calcium oxide on the physical character of the soil is also discussed.   H. B. H.

The Nitrogen Distribution of Fibrin Hydrolysed in the Presence of Ferric Chloride. CLARENCE AUSTIN MORROW and WALTER RAYMOND FETZER (*Soil Sci.*, 1918, **5**, 163—167).—With the view of obtaining more evidence on the formation of humin nitrogen in soils, fibrin was hydrolysed (1) alone, (2) in the presence of ten times its weight of anhydrous ferric chloride, and the resulting product was, in each case, analysed by the Van Slyke method. The results show that when a protein is hydrolysed in the presence of ferric chloride, an accurate nitrogen distribution cannot be obtained. There is a substantial increase in the ammonia nitrogen (from 10·48 to 13·17%), due to the presence of ferric chloride, owing probably to the higher temperature of hydrolysis, and consequent deamination of some amino-acids. The acid-soluble humin nitrogen increases (from 1·0 to 9·84%) at the expense of a corresponding loss in the filtrate from the bases. The earlier conclusion (compare A., 1917, i, 512) in regard to humin nitrogen precipitated by calcium hydroxide is therefore incorrect, a part of this acid-soluble humin being of protein origin instead of largely non-protein. Emphasis is laid on the fact that much of the recent work on the organic nitrogen distribution in soils by Van Slyke's method is entirely untrustworthy. [See also *Ind.*, May.]

W. G.

The Significance of the Sulphur in Ammonium Sulphate Applied to certain Soils. CHARLES B. LIPMAN and W. F. GERICKE (*Soil Sci.*, 1918, **5**, 81—86).—The superiority of ammonium sulphate as a nitrogenous fertiliser for barley (compare *ibid.*, 1916, **2**, 575) is apparently due to its sulphur content, the sulphur combined with the nitrogen producing the effect. [See, further, *Ind.*, 252A.]

W. G.

Some Availability Studies with Ammonium Phosphate and its Chemical and Biological Effects on the Soil. F. E. ALLISON (*Soil Sci.*, 1918, **5**, 1—80).—A comparison of commercial ammonium phosphate with ammonium sulphate, organic fertilisers, and certain phosphatic fertilisers. Ammonium phosphate nitrifies at approximately the same rate as ammonium sulphate, whilst organic nitrogenous manures, such as dried blood and cottonseed meal, are much less available. Calcium carbonate proved favourable to nitrification, but calcium oxide sometimes caused a depression in the nitrification of the two ammonium salts. There was apparently but little difference in the availability of the phosphorus in ammonium phosphate, acid phosphate, and basic slag, but raw rock phosphate was much less available.

For details of manufacture of the ammonium phosphate and comparative cropping tests with the various fertilisers, see *Ind.*, 252A.

W. G.

Organic Chemistry.

Revision of the Tables for the Strength of Ethyl Alcohol.
N. Schoorl and (Miss) A. Regenbogen (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 831—837, and *Pharm. Weekblad*, 1918, **55**, 390—409).—In view of the preparation of a new edition of the Dutch Pharmacopœia, measurements have been made of the density of mixtures of ethyl alcohol and water at 15°. The results obtained are in agreement with those obtained by Osborne and MacKelvy (compare A., 1912, i, 232), and the authors recommend the table of the Bureau of Standards (Washington) as affording the most accurate values of the densities of alcohol–water mixtures. [See also *J. Soc. Chem. Ind.*, 318A.]   H. M. D.

Preparation of Amylene Bromohydrin (Bromoamyl Alcohol). Emil Rath (D.R.-P., 301905 ; from *Chem. Zentr.*, 1918, i, 53).—Mixtures of hypobromites and such acids as boric acid yield with amylene (β-methyl-Δ^β^-butylene) in the cold the bromohydrin, which may be useful in the production of pharmaceutical preparations.   J. C. W.

New Molybdyl Compound. Ricardo Montequi Díaz de Plaza (*Anal. Fís. Quim.*, 1910, **14**, 542—548; from *Chem. Abstr.*, 1917, **11**, 2864—2865).—When aqueous solutions of ammonium molybdate and potassium *iso*butylxanthate are mixed, the liquid after a time assumes a dark violet colour, and when acidified by the gradual addition of acetic acid, a dark-coloured substance, consisting of a mixture of $(C_5H_9OS_2)_4,Mo_2O_3$ and $(C_5H_9OS_2)_2$, is precipitated. When the precipitate is dried and extracted with light petroleum, the latter substance is removed.

The molybdenum compound forms nearly black, monoclinic crystals, m. p. 105°, insoluble in water, slightly soluble with purple colour in cold, and with greenish-blue colour in hot, ethyl alcohol, and readily soluble in acetone, benzene, toluene, carbon disulphide, chloroform, or ethyl ether with intense purple coloration. It is not acted on in the cold by concentrated hydrochloric or sulphuric acid. It is oxidised by nitric acid, and dissolves readily in potassium hydroxide solution, but not in ammonia.   H. M. D.

Configuration of Organic Compounds and their Relation to Chemical and Physical Properties. Arthur Michael (*J. Amer. Chem. Soc.*, 1918, **40**, 704—723).—A theoretical paper in which the author discusses the relationships between the free and bound energy, and entropy changes with the spacial arrangement of the atoms in stereoisomerides. The influence of olefinoid unsaturation and configuration on the affinity constants of acids is discussed in the cases of aliphatic acids, dibasic unsaturated acids, and the cinnamic acids.   J. F. S.

Relative Stabilities of Halogen-substituted Aliphatic Acids in Aqueous Solution. II. The Propionic and Butyric Acid Series. G. S. Simpson (*J. Amer. Chem. Soc.*, 1918, **40**, 674—683. Compare this vol., i, 57).—The hydroxylation of halogen derivatives of propionic and butyric acids has been studied by keeping $0.1N$-solutions of their sodium salts at 70° and titrating the sodium haloid formed at different intervals. The following order of stability is established:—*propionic* acid series: β-bromo-, β-iodo-, α-bromo-, β-chloro-, αα-dibromo-, αβ-dibromo-, α-chloro-, αβ-dichloro-, of the order 1, 1·03, 3·31, 7·17, 10·96, 18·68, 37·06, 186·8; *butyric* acid series: α-bromo*iso*-, β-chloro-, α-bromo-, α-chloro-, of the order 1, 277, 374, 6171.

From these figures, the following points are apparent: (1) chlorine-substituted acids are more stable than analogous bromine or iodine compounds; (2) iodine compounds are sometimes more stable than bromine analogues; (3) α-halogen acids are more stable than their β-isomerides, and position is of greater moment than the nature of the halogen; (4) if the hydrogen atoms in the –CH₂Hal. or –CHHal.– groups are replaced by alkyl radicles, the stability of the acids is diminished, and the larger the alkyl group, the greater is the weakening effect; (5) a second halogen atom in the α-position renders the removal of a halogen in the α- or β-position more difficult.

Some brief notes on the preparation of the various acids are given, and the bearing of some of the results on problems connected with the hydrolysis of the salts (compare Senter and others) is discussed.   J. C. W.

Synthesis and Oxidation of Tertiary Hydrocarbons. P. A. Levene and L. H. Cretcher, jun. (*J. Biol. Chem.*, 1918, **33**, 505—512).—The tertiary hydrocarbons are prepared by the reduction of acids obtained by the malonic ester synthesis.

Ethyl dibutylmalonate, $C(C_4H_9)_2(CO_2Et)_2$, is formed by the action of butyl iodide and sodium ethoxide on ethyl malonate. The introduction of the first butyl radicle must be completed before that of the second is attempted. The attempt to effect both substitutions at the same time by heating the malonic ester with two molecules of the ethoxide and iodide gives unsatisfactory results. Ethyl dibutylmalonate boils at 153—154°/14 mm. (corr.). On saponification, *dibutylmalonic acid*, $C_{11}H_{20}O_4$, is obtained. It crystallises from benzene in long, prismatic needles, m. p. 163° (decomp.). On heating at 180°, carbon dioxide is evolved, and at 255° (corr.), *α-butylhexoic acid*, $CH(C_4H_9)_2 \cdot CO_2H$, distils over; this has b. p. 153°/16 mm. and D^{16} 0·899. The ester, *ethyl α-butylhexoate*, $C_{12}H_{24}O_2$, is prepared by boiling the acid with alcohol and a little sulphuric acid for eight hours, and has b. p. 114—115°/15 mm. (corr.). The reduction of the ester to the corresponding alcohol is accomplished by Levene and Allen's method (A., 1917, i, 3), the yield being 65 to 70% of that theoretically possible. *β-Butylhexyl alcohol*, $C_{10}H_{22}O$, has b. p. 218—219°

(corr.) and D 0·836. On boiling the alcohol with three molecules of hydriodic acid for five hours, an 80% yield of *β-butylhexyl iodide*, $C_{10}H_{21}I$, is obtained, b. p. 124—125°/13 mm., D 1·267, and reduction of the iodide with zinc and glacial acetic acid yields *β-butylhexane*, $C_{10}H_{22}$, b. p. 165° (corr.), D 0·738.

When β-butylhexyl iodide is slowly added to an excess of the monosodium derivative of ethyl malonate in alcohol and the mixture boiled, *ethyl β-butylhexylmalonate*, $C_{17}H_{32}O_4$, b. p. 180°/14 mm., is produced, which on saponification yields *β-butylhexyl-malonic acid*, $C_{13}H_{24}O_4$, rhombic needles from light petroleum, m. p. 88° (corr.). The following compounds are prepared by the methods already indicated in the case of the β-butylhexane derivatives: *γ-butyloctoic acid*, $C_{12}H_{24}O_2$, b. p. 173—174°/12 mm. (corr.), D 0·901; *ethyl γ-butyloctoate*, $C_{14}H_{28}O_2$, b. p. 139°/10 mm. (corr.); *δ-butyloctyl alcohol*, $C_{12}H_{26}O$, b. p. 139°/15 mm., D 0·841; and *δ-butyloctyl iodide*, $C_{12}H_{25}I$, b. p. 143°/8 mm., D 1·194.

β-Butylhexane is readily oxidised at 80—90° by an alkaline solution of permanganate, but the only oxidation products which can be detected are formic acid and carbon dioxide. At 25°, a small amount of butyric acid is formed, which is recognised by its silver salt.   H. W. B.

Preparation of Acetaldehyde. H. DREYFUS (Brit. Pat. 105064).—Acetylene which has been freed from such impurities as hydrogen sulphide, hydrogen phosphide, and ammonia, is passed, under a pressure of about 1·5 atm., into a solution containing 10—15% of sulphuric acid and from 1 to 10%, preferably 3—6%, of mercury. The liquid is kept at 25—40°, and the gas is passed *in* slowly, with vigorous agitation, until the precipitated mercury compound becomes grey or greyish-black, and then as rapidly as the liquid will absorb it. At intervals, the temperature is raised to not above 50—60° to distil off the acetaldehyde. A yield of acetaldehyde equivalent to 90—95% of the quantity of acetylene, or five to ten times that of the mercury compound used, is obtained. [See, further, *J. Soc. Chem. Ind.*, 1918, 222A.]   A. S.

The Crotonisation of Acetaldehyde. Formation of Butanol and Hexanol from Ethyl Alcohol. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1918, **166**, 632—636).— Acetaldehyde when passed over the oxides of thorium, titanium, or uranium at 360° undergoes crotonisation and gives croton-aldehyde, hexadienaldehyde, and a certain amount of higher homologues. If ethyl alcohol is used as the starting material, it is passed first over reduced copper at 300°, and the resulting vapours are then passed over uranium oxide at 360°, or the vapours of the alcohol may be passed slowly over uranium oxide at 360°, when they undergo dehydrogenation and dehydration in the one process. The best yield of crotonaldehyde is obtained by vaporising paracetaldehyde and passing these vapours over the catalyst. If the products of the crotonisation are roughly fractionally distilled and the fractions boiling at about 90—130° and 130—220° passed

*p**

with hydrogen over reduced nickel at 170—180°, normal butyl alcohol and normal hexanol are obtained.   W. G.

Acetone and Lime. M. E. FREUDENHEIM (*J. Physical Chem.*, 1918, **22**, 184—193).—When acetone vapour is passed over slaked lime in a tube heated at temperatures varying from 350° to 630°, calcium carbonate and carbon are left in the tube, the amount of carbon being small at low temperatures, but rapidly increasing with a rise in temperature. The gas evolved consists of methane, hydrogen, carbon monoxide, ethylene, and carbon dioxide. The amount of gas decreases during the run, and the percentage of hydrogen also shows a tendency to decrease, whilst the percentage of methane increases; the percentages of carbon monoxide and olefines remain practically constant at 16% and 4% respectively. At 350°, the gaseous products are nearly 80% hydrogen and 20% methane; at 650° methane is the chief gaseous product.

It is thought that acetone may be an intermediate product of the action of lime on calcium acetate, and that its dissociation may account for the presence of carbon monoxide, thus: $CH_3 \cdot CO \cdot CH_3 = CH_4 + CO + C + H_2$, whilst the ethylene may owe its formation to the production of methane and keten, the latter breaking down into carbon monoxide and ethylene, thus: $CH_3 \cdot CO \cdot CH_3 = CH_4 + CH_2 : CO$, $2CH_2 : CO = 2CO + C_2H_4$. The production of hydrogen and methane only at 350° cannot be accounted for satisfactorily, though it is known that hydrogen is also set free when sodium acetate is heated with soda lime.

When acetone is passed over heated nickel, carbon is precipitated and some of the excess of acetone is reduced to *iso*propyl alcohol, and it is stated that the decreasing percentage of hydrogen evolved at higher temperatures is probably due to its action on the acetone, with formation of *iso*propyl alcohol. [See also *J. Soc. Chem. Ind.*, 282A.]   B. N.

Synthesis of Two Isomeric Series of Alkylthioglucosides. WILHELM SCHNEIDER, JOHANNA SEPP, and OTTILIE STIEHLER (*Ber.*, 1918, **51**, 220—234. Compare A., 1916, i, 792).—The reaction by which glucose mercaptals may be converted into alkylthioglucosides, namely, by treatment with one molecular proportion of mercuric chloride, has been extended from the ethyl to the methyl, *n*-propyl, and benzyl compounds. The products obtained in this way happen to be all α-glucosides, but the isomeric β-glucosides can also be formed, the mode of preparation depending on the interaction of the potassium salts of mercaptans with acetobromoglucose. Compared with the α- and β-methylglucosides, the two series of thioglucosides show a remarkable difference; the β-isomerides are much more stable towards dilute mineral acids than the α-compounds in this case. The thioglucosides are also non-acidic, whereas the mercaptals dissolve in alkali hydroxides.

The new mercaptals were again prepared by Fischer's method, namely, condensation of glucose with the thiol under the influence

of concentrated hydrochloric acid. *Glucose methyl mercaptal*, $C_6H_{12}O_5(SMe)_2$, has m. p. 161°, $[\alpha]_D^{24}$ in N-sodium hydroxide, $-20\cdot76°$, and forms a *penta-acetate*, m. p. 83°, $[\alpha]_D^{20}$ in *s*-tetrachloroethane, $+38\cdot71°$; *α-methylthioglucoside*, $C_6H_{11}O_5\cdot SMe$, crystallises in slender needles, m. p. 137°, $[\alpha]_D^{30}$ in water, $+124\cdot5°$, and its *tetra-acetate* has m. p. 89°, $[\alpha]_D^{23}$ in *s*-tetrachloroethane, $+150\cdot0$. *Penta-acetylglucose ethyl mercaptal*, m. p. 42—45°, $[\alpha]_D^{20} +17\cdot71°$, is very stable towards mercuric chloride, and cannot be converted by its agency into the tetra-acetyl derivative of true, aldehydic glucose. *Glucose* n-*propyl mercaptal* forms slender leaflets, m. p. 146°, and *α-n-propylthioglucoside* has m. p. 118—122°, $[\alpha]_D^{24}$ in water, $+116\cdot5°$. *α-Benzylthioglucoside* has m. p. 112—114° (viscous), 118° (mobile), $[\alpha]_D^{25} +175\cdot7°$, and forms a *tetra-acetate*, prismatic needles, m. p. 77°, $[\alpha]_D^{23} +186\cdot3°$; *penta-acetylglucose benzyl mercaptal* has m. p. 64°, $[\alpha]_D^{22} +31\cdot75°$.

The hydrolysis of α-ethylthioglucoside has been examined. It is unaffected by maltase, emulsin, or myrosin; with 1% hydrochloric acid at 25°, equilibrium is reached in thirty-four hours, when 94—95% has been hydrolysed, but with 2·5% hydrochloric acid, the same result is obtained in eight to nine hours.

Acetobromoglucose and potassium methyl sulphide react in methyl-alcoholic solution to form *tetra-acetyl-β-methylthioglucoside*, slender needles, m. p. 93°, $[\alpha]_D^{20}$ in *s*-tetrachloroethane, $-14\cdot67°$, which is hydrolysed by barium hydroxide solution in the cold to *β-methylthioglucoside*, a syrup with $[\alpha]_D^{15} -18\cdot14°$. Partial hydrolysis takes place in the first stage, so the crude product is heated with acetic anhydride and sodium acetate before purification. *Tetra-acetyl-β-ethylthioglucoside* crystallises in needles, m. p. 78—79°, $[\alpha]_D^{20} -22\cdot27°$, and forms a compound, m. p. 83—84°, with ordinary tetra-acetyl-β-ethylglucoside; *β-ethylthioglucoside* forms stout, rectangular prisms, $1H_2O$, m. p. 46—47°, the anhydrous substance having m. p. 99—100°, $[\alpha]_D^{25} -55\cdot14°$. *Tetra-acetyl-β-benzylthioglucoside* has m. p. 98°, $[\alpha]_D^{24} -93\cdot1°$, and *β-benzylthioglucoside* is a syrup.

β-Ethylthioglucoside is unaffected by emulsin, myrosin, or maltase, and is not perceptibly altered by hydrochloric acid unless the concentration is at least 5% and the temperature 70—80°.

J. C. W.

Structure of Crystalline β-Methylfructoside. ETTIE STEWART STEELE (T., 1918, **113**, 257—263).—Recent investigations (Irvine and Robertson, A., 1917, i, 79) have shown that it is very probable that the syrup obtained by condensing fructose with methyl alcohol contains the α- and β-modifications of both butylene-oxidic and ethylene-oxidic methylfructosides. The mixture may be methylated by means of silver oxide and methyl iodide, and the product converted by hydrolysis into a mixture of tetramethylfructoses, consisting of a crystalline and a syrupy variety (Purdie and Paul, T., 1907, **91**, 289). The same crystalline tetramethylfructose has now been obtained by similar treatment of Hudson's

crystalline β-methylfructoside (A., 1916, i, 547), which is stable towards permanganate, that is, conforms to the butylene oxide type. The crystalline tetramethylfructose must therefore be butylene-oxidic, or, in other words, the original mixture of β-methylfructosides contains Hudson's γ-oxidic isomeride.

The action of acetic anhydride on fructose, in the presence of zinc chloride, yields about equal quantities of crystalline and syrupy products. The solid portion is stable towards permanganate, and is the tetra-acetate from which Hudson prepared his β-methylfructoside. It may be acetylated completely, and is derived, therefore, from butylene-oxidic fructose. The syrup is apparently a triacetate, which resists further acetylation, may be converted into a mono-methyl ether (not a methylfructoside triacetate), and very readily reduces permanganate. It is therefore derived from ethylene-oxidic fructose. J. C. W.

Preparation of a Salt of Fructosediphosphoric Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 302094; from *Chem. Zentr.*, 1918, i, 249).—The calcium salt of fructosediphosphoric acid (from metaphosphoric esters and fructose) is only sparingly soluble, but is, nevertheless, easily absorbed in the organism, and is claimed to be good in such cases as rickets.

J. C. W.

The Digestibility of Bread. III. Erythrodextrin in Starch Hydrolysis. J. C. BLAKE (*J. Amer. Chem. Soc.*, 1918, **40**, 623—636. Compare A., 1916, i, 578; 1917, i, 361).—In the previous communication, it was shown that the digestion of erythrodextrin is a unimolecular reaction. It might therefore be used in order to determine amylolytic activity, and, consequently, efforts have been made to obtain pure erythrodextrin for such purposes. In this connexion, the present paper describes some new studies on the degradation of starch by (*a*) heating starch moistened with 0·1N-hydrochloric acid at 85°, and (*b*) boiling starch with about 0·032N-hydrochloric acid, and also new methods for estimating the products by measuring the colorations produced by iodine water. It is expected that it will soon be possible to prepare pure erythrodextrin.

It appears that the cleavage of boiled starch takes place in at least three stages, protein and amylodextrin preceding erythramylum (rose-amylose) and erythrodextrin in order of formation. These stages probably correspond with the stages of salivary digestion and the degradation by roasting.

A number of supplementary notes are recorded. (1) "Artificial starch," the substance which crystallises at about 50° on cooling a partly hydrolysed solution of starch, is a solid solution of amylodextrin and erythrodextrin in higher polysaccharides. (2) Lintner's "soluble starch" is almost pure amylodextrin, crystallising with difficulty only at temperatures below 50°, and forming an iodide, the transition temperature of which, in 1% solutions, is 69·5°. (3) Amylodextrin appears to be an individual substance, fairly

soluble in cold water, but not in 40% alcohol; it gives a blue iodide which has the maximum transition point, 74°; it probably yields erythrodextrin on hydrolysis. (4) Erythrodextrin is insoluble in 49—67% alcohol; the transition point of its iodide is 64°; it yields achroodextrin on hydrolysis, but in the "roasting" process it appears to be the final polysaccharide. (5) Erythramylum is formed simultaneously with erythrodextrin, and probably changes into amylodextrin on hydrolysis; it is precipitated by 35% alcohol.

<div align="right">J. C. W.</div>

Preparation of Taurine in Large Quantities. CARL L. A. SCHMIDT and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 499—500).—Taurine is readily prepared from the abalone, *Haliotis*, which can be obtained in quantity on the Pacific coast. The shell and intestinal tract are removed, and the muscle is then finely minced and the juice pressed out. Protein is removed from the juice by precipitation with acetic acid, and the filtrate hydrolysed with hydrochloric acid. After concentration, the taurine is precipitated by alcohol, and finally recrystallised from water. Eight dozen abalones (74 kilograms of muscle) yield 362 grams of taurine.

<div align="right">H. W. B.</div>

Interaction of Formaldehyde and Carbamide. AUGUSTUS EDWARD DIXON (T., 1918, **113**, 238—248).—A number of experiments on the condensation of carbamide with formaldehyde (37·5% solution) are described. Equimolecular proportions, just neutralised with dilute sodium hydroxide, yield on evaporation in a desiccator methylolcarbamide, $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot OH$, which gives no reaction for formaldehyde unless acidified. With a double proportion of formaldehyde, under the same conditions, the product is dimethylolcarbamide, $CO(NH \cdot CH_2 \cdot OH)_2$, which changes at about 123° or when treated with dilute hydrochloric acid into the compound, $CO<^{NH \underline{\hspace{2em}} CH_2 \cdot NH}_{N(CH_2 \cdot OH) \cdot CH_2 \cdot NH}>CO$, thus, $2C_3H_8O_3N_2 \longrightarrow C_5H_{10}O_3N_4 + CH_2O + 2H_2O$. The two methylol derivatives have already been described by Einhorn and Hamburger (A., 1908, i, 141), and the third product is Goldschmidt's compound (A., 1897, i, 22; 1898, i, 178).

When condensation between formaldehyde and carbamide is catalysed by small quantities of acids, granular precipitates usually appear very quickly. They vary in composition, but display as a common feature black crosses in plane polarised light. With 0·75 mol. of formaldehyde, the product is dimeric methylene-carbamide, presumably formed, in the presence of small quantities of acids, from the initial methylolcarbamide, thus:

$$NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot OH \longrightarrow NH_2 \cdot CO \cdot NH \cdot CH_2X \longrightarrow$$

$$HX + \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot \longrightarrow CO<^{NH \cdot CH_2 \cdot NH}_{NH \cdot CH_2 \cdot NH}>CO$$
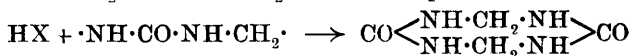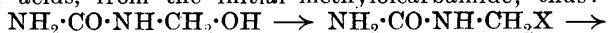
With 1·5 to more than 2 mols., the sole product is Goldschmidt's compound, probably formed by the action of formaldehyde on

"nascent" monomeric methylenecarbamide. With 4 mols., the precipitate is scanty and consists of a substance probably of the formula $CH_2(NH \cdot CO \cdot NH \cdot CH_2 \cdot OH)_2$, whilst with 11 mols. condensation ceases. J. C. W.

Thiocyanates and Thiocarbimides. XII. The Polyketide Thiocarbimide, Ethyl α-Thiocarbiminopropionate. TREAT B. JOHNSON and ARTHUR A. TICKNOR (*J. Amer. Chem. Soc.*, 1900, **40**, 636—646. Compare A., 1916, i, 635, 717).— Inactive ethyl α-thiocyanopropionate (I) was prepared by Wheeler and Barnes from the α-bromopropionate and potassium thiocyanate (A., 1900, i, 566). The inactive and dextrorotatory forms of the isomeric ethyl α-thiocarbiminopropionate (II) have now been obtained by the interaction of thiocarbonyl chloride and the ethyl α-aminopropionates.

$$N{:}C \cdot S \cdot CHMe \cdot CO_2Et \qquad\qquad S{:}C{:}N \cdot CHMe \cdot CO_2Et$$
$$\text{(I.)} \qquad\qquad\qquad \text{(II.)}$$
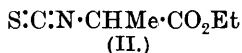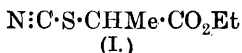
Racemic alanine hydrochloride is most conveniently prepared by conducting the crude acetaldehyde from the oxidation of alcohol directly into a solution of commercial sodium cyanide, ammonium chloride, and ammonia, and after twenty-four hours acidifying and evaporating to dryness. The free ester (3 mols.) reacts vigorously with thiocarbonyl chloride (1 mol.) in dry ether, and the hydrochloride reacts with rather more than one molecular proportion of thiocarbonyl chloride in boiling toluene, giving the *hydrochloride* of *ethyl* dl-α-*thiocarbiminopropionate*, m. p. 87°. The free *ester*, obtained on distillation of the salt, is a pale yellow oil, b. p. 93·5—94·5°/13 mm., D 1·0994 (average), n_D^{20} 1·4915. Similarly, active alanine ester hydrochloride gives rise to *ethyl* d-α-*thiocarbiminopropionate*, b. p. 100—101°/11—12 mm., n_D^{20} 1·4935, $[\alpha]_D^{20} +29·77°$, but the free amino-acid does not react in this way.

As a thiocarbimide, the inactive ester reacts with aniline to form *ethyl phenyl-α-methylthiohydantoate*,
$$NHPh \cdot CS \cdot NH \cdot CHMe \cdot CO_2Et,$$
which crystallises in rosettes, m. p. 83—84°. Inactive ethyl alanine and phenylthiocarbimide apparently produce the same compound, but the reaction is so vigorous that this loses alcohol, and so the actual product is 2-*thio-1-phenyl-4-methylhydantoin*,
$$CS{<}^{NPh \cdot CO}_{NH—CHMe},$$ m. p. 183·5—184·5° (compare Aschan, A., 1883, 1107).
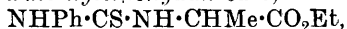
Furthermore, the ester reacts with hot alcohol to form the *thionurethane*, $OEt \cdot CS \cdot NH \cdot CHMe \cdot CO_2Et$, in slender prisms, m. p. 55·5—56°, b. p. 157—159°/18 mm. J. C. W.

New Preparation of Nitriles by Catalysis of Primary Amines. ALPH. MAILHE and F. DE GODON (*J. Pharm. Chim.*, 1917, [vii], **16**, 225—229).—A claim for priority over Sabatier and

Gaudion (compare A., 1917, ii, 460) for the use of reduced copper or reduced nickel as catalysts for the conversion of primary amines into the corresponding nitriles. The present authors had deposited the details of their process in a sealed communication in March, 1917. W. G.

Preparation of Halogenated Arsinic Acids. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 296915; from *Chem. Zentr.*, 1917, i, 715).—Hydrocarbons of the acetylene series are treated with arsenic trihaloids, or mixtures which yield these compounds, and the products are converted into arsenoxides and then into arsinic acids by oxidation. Thus, heptinene gives "heptinene-chloroarsenoxide," a dark syrup, and "*heptinenechloroarsinic acid*" [?, β-*chloro*-Δ^α-*heptenylarsinic acid*, $C_5H_{11}\cdot CCl:CH\cdot AsO(OH)_2$], white needles, m. p. 115°, the sodium salt of which is freely soluble in water. Octinene yields "octinenebromoarsenoxide" and "octinenebromoarsinic acid" [?, β-*bromo*-Δ^α-*octenylarsinic acid*], m. p. 129—130°. J. C. W.

Werner's Theory of Valency and Benzene. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 400—405).—The author is of opinion that Werner's theory of valency is not adapted to account for the structure and properties of benzene and its derivatives.
A. J. W.

Sulphite Turpentine. A. W. SCHORGER (*J. Ind. Eng. Chem.*, 1918, **10**, 258—260).—The so-called sulphite turpentine, obtained as a by-product in the manufacture of wood pulp by the sulphite process, consists in the main of cymene, and may be utilised in the production of toluene and carvacrol. Cymene-2-sulphonic acid forms a characteristic barium salt, $(C_{10}H_{13}SO_3)_2Ba,3H_2O$, which is sparingly soluble in water and crystallises in lustrous plates. On heating the anhydrous barium salt of the 2-sulphonic acid with an equal weight of phosphorus pentachloride, and forming the amide by heating with ammonia, a yield of 70·7 per cent. of the theoretical amount of cymenesulphonamide, m. p. 114°, was obtained. By oxidation with potassium permanganate, the cymene was converted into *p*-hydroxy*iso*propylbenzoic acid, m. p. 155°. Cymene also reacts readily with chlorosulphonic acid, and the resulting product may be converted into the sulphonamide by heating it with strong ammonia solution on the boiling water-bath. This reaction affords a convenient method of identifying pure cymene. When the sodium salt of cymene-2-sulphonic acid is fused with alkali at about 300°, carvacrol is produced in small quantity, and may be purified by converting it into carvacrol nitrite, m. p. 150—152°, which is insoluble in light petroleum. [See also *J. Soc. Chem. Ind.*, 296A.] C. A. M.

Steric Hindrance. IV. J. VON BRAUN, Z. ARKUSZEWSKI, and Z. KÖHLER (*Ber.*, 1918, **51**, 282—296).—Comparing dimethyl-*o*-

toluidine (I) with 1:8-dimethyltetrahydroquinoline (II), von Braun was surprised to find that the retarding influence of the o-methyl group on the reactivity of the nitrogen atom and the carbon atom opposite to it is considerably less in II than in I (A., 1916, i, 647). It is now found that when the methyl group is extended to a ring, as in III, its influence is also very much less.
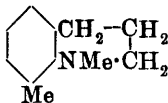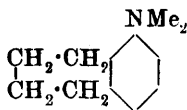
(I.)   (II.)   (III.)

5 : 6 : 7 : 8-Tetrahydro-α-naphthyldimethylamine (III) (Bamberger and Helwig, A., 1889, 891) reacts with methyl iodide more readily than dimethyl-o-toluidine, and when warmed with cyanogen bromide yields the *tetrahydro-α-naphthylcyanomethylamine*, b. p. 179—180°/7 mm., which may be hydrolysed by boiling with 25% hydrochloric acid to 5:6:7:8-*tetrahydro-α-naphthylmethylamine*, a pale yellow oil, b. p. 150—152°/12 mm. (*picrate*, m. p. 174°; *thiocarbamide* derivative, m. p. 113°). The base also reacts with formaldehyde, giving, after twenty-four hours' warming with formalin and concentrated hydrochloric acid, 4-*hydroxymethyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthyldimethylamine* (annexed formula), as a very viscous, yellow oil, b. p. 189—196°/10 mm. (*picrate*, m. p. 92—94°). Further reactivities of the para-carbon atom are exhibited by the formation of a nitroso-compound (*ibid.*) and by coupling with diazotised sulphanilic acid.
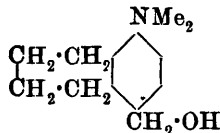
This weakening of the influence of the o-methyl group is not due to ring formation, as was previously supposed, for whilst dimethyl-2-m-xylidine (IV) is even less reactive than dimethyl-o-toluidine, dimethyl-2-p-xylidine (VI) is more reactive, and dimethyl-3-o-xylidine (V) is more reactive still.
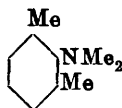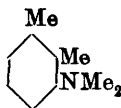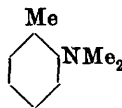
(IV.)   (V.)   (VI.)

Thus, dimethyl-3-o-xylidine forms about three times as much methiodide in a given time as dimethyl-o-toluidine; when warmed with zinc chloride and benzaldehyde for five minutes and then mixed with chloranil, it gives a distinct malachite-green colour, and when heated with "formalin" and concentrated hydrochloric acid, it yields 4-*dimethylamino*-2 : 3-*dimethylbenzyl alcohol*,

$$NMe_2 \cdot C_6H_2Me_2 \cdot CH_2 \cdot OH,$$

b. p. 149—152°/5 mm. (*picrate*, m. p. 112°; *platinichloride*, m. p. 192°; *methiodide*, m. p. 176°).

Similarly, *dimethyl-2-p-xylidine* (VI), b. p. 204° (*picrate*, m. p. 158°; *platinichloride*, m. p. 196°) reacts almost as sluggishly as dimethyl-*o*-toluidine with methyl iodide, forming the *methiodide*, m. p. 202°, but yields *4-dimethylamino-2:5-dimethylbenzyl alcohol* when condensed with formaldehyde, this being a pale yellow, very viscous oil, b. p. 168—170°/20 mm., which gives a *picrate*, m. p. 114°, a *methiodide*, m. p. 180°, and a *platinichloride*, m. p. 188°.

The conclusion is therefore drawn that the nitrogen atom and para-carbon atom are so inert in dimethyl-*o*-toluidine because the *o*-methyl group and the nitrogen atom are linked by residual affinity. This link is weakened if a meta-substituent is introduced, as the ortho- and meta-groups will then be similarly united, and the nitrogen atom will be more free to react. There is not so much likelihood of a union between a para-substituent and the nitrogen atom, and therefore a meta-group should not have much influence on the activities of a para-substituted tertiary amine. This point has been tested in the case of the base (annexed formula), which actually resembles dimethyl-*p*-toluidine in reactions.

$CH_2 \big<{}^{CH_2}_{CH_2}$ NMe$_2$
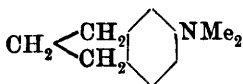
The base is synthesised as follows: technical indene is hydrogenated in the presence of palladous chloride, the hydrindene is nitrated at $-5°$, the mixture of much *m*- with little *o*-nitrohydrindene is reduced with iron powder and acetic acid, and the mixture of primary amines is warmed with methyl iodide and sodium carbonate. A small quantity of o-*dimethylaminohydrindene*, b. p. 130—131°/20 mm. (*picrate*, m. p. 147°; *platinichloride*, m. p. 185—186°; *methiodide*, m. p. 202°), is formed, but the main product is the *quaternary iodide*, leaflets, m. p. 190°, of the desired m-*dimethylaminohydrindene* (above). This is obtained by distilling the methiodide, as an oil, b. p. 136—138°/18 mm., which forms a *picrate*, m. p. 160—161°, a *platinichloride*, m. p. 170—175°, a red *nitro*-compound, m. p. 85—86°, and a *thiocarbamide* derivative, m. p. 118°, and reacts with formaldehyde and concentrated hydrochloric acid to yield

$CH_2 \big<{}^{CH_2}_{CH_2}$ CH$_2$·OH / NMe$_2$
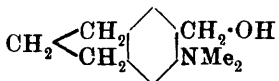
5 - *dimethylamino* - 6 - *hydroxymethylhydrindene* (annexed formula). The latter is a very viscous, pale yellow liquid, b. p. 200°/31 mm., which gives a *picrate*, m. p. 144°, a *platinichloride*, m. p. 178° (decomp.), and a *methiodide*, m. p. 177°.   J. C. W.

Preparation of Tertiary Amines. OSKAR MATTER (D.-R.P., 301450 and 301832; from *Chem. Zentr.*, 1918, i, 53, 149).— Chlorine derivatives of the hydrocarbons are heated with sodamide, the mixture being stirred, and, if necessary, agents like copper gauze or copper powder being employed as catalysts. Thus, chlorobenzene yields triphenylamine, benzyl chloride at 110—120° gives

p^{**}

tribenzylamine, and *iso*amyl chloride at 210—220° forms tri*iso*-amylamine.

Mixtures of the chlorine compound and a primary amine may also be heated with sodamide, when, if the amine contains a different radicle, a mixed *tert.*-amine results. Thus, benzyl chloride, benzylamine, and sodamide, at 100—110°, yield tribenzyl-amine, benzyl chloride and aniline produce dibenzylaniline, and benzyl chloride and *p*-toluidine give dibenzyl-*p*-toluidine.

J. C. W.

Preparation of a Sparingly Soluble Complex Compound from Dimethylaniline, Benzyl Chloride, and Zinc Chloride. CHEMICAL WORKS, ROHNER & CO. (Brit. Pat. 104676).—A mixture of one molecular proportion of benzyl chloride and of dimethyl-aniline respectively is stirred with an aqueous solution of rather more than half a molecular proportion of zinc chloride until the separation of crystals of phenylbenzyldimethylammonium zinci-chloride is complete.   A. S.

Separation of Cresols. G. A. DARZENS (Brit. Pat. 107961).—*p*-Cresol and *m*-cresol are separated from mixtures by converting them into additive products with oxalic acid and with anhydrous sodium acetate respectively in the presence of a suitable solvent and with exclusion of moisture. The additive product is separated by filtration and subsequently decomposed by water. If *o*-cresol is also present, it is separated by a preliminary fractional dis-tillation in a vacuum. [See, further, *J. Soc. Chem. Ind.*, 1918, 235A.]   A. S.

Preparation of Carbamic Esters and their N-Alkyl Derivatives, and Carbonic Esters. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P., 296889; from *Chem. Zentr.*, 1917, i, 714).—Homologues of phenol, except the cresols, are converted into carbonates or carbamates in the usual way. The products are odourless and tasteless, and have anthelmintic properties. Thus, *p-tert.*-butylphenol reacts with carbonyl chloride to form p-tert.-*butylphenyl carbonate*, $CO(O \cdot C_6H_4 \cdot CMe_3)_2$, m. p. 108°, in the presence of pyridine, and p-tert.-*butylphenyl* N-*dimethylcarb-amate*, $NMe_2 \cdot CO_2 \cdot C_6H_4 \cdot CMe_3$, m. p. 92°, in the presence of dimethylamine, whilst the corresponding *carbamate* crystallises in platelets or needles, m. p. 123—124°. p-iso*Amylphenyl carbamate* has m. p. 73—74°, p-*benzylphenyl carbamate*, m. p. 144°, p-iso-*propylphenyl carbamate*, m. p. 93—95°, and o-*allylphenyl carb-amate*, m. p. 122—123°.   J. C. W.

[*p*-**Benzylphenyl Carbamate.**] SYNTHETIC PATENTS CO. (U.S. Pat. 1252452).—The carbonyl derivatives of phenols, of the general formula $R \cdot C_6H_4 \cdot O \cdot CO \cdot R'$, in which R is a substituent with more than one carbon atom and R' is $O \cdot C_6H_4R$ or NXX', X and X' being respectively either a hydrogen atom or an alkyl

group, are white powders, practically tasteless and odourless, generally sparingly soluble in water, and of value as anthelmintic remedies. *p*-Benzylphenyl carbamate, crystals (from alcohol), m. p. 144°, is specifically claimed. *p*-Butylphenyl carbonate melts at 108°, *p-iso*amylphenyl carbamate at 73—74°, *p*-butylphenyl carbamate at 123—124°, *p-iso*propylphenyl carbamate at 93—95°, *p*-butylphenyl *N*-dimethylcarbamate at 92°, and *o*-allylphenyl carbamate at 122—123°. A. S.

Synthesis of 3 : 4-Dihydroxyphenanthrene (Morphol) and of 3 : 4-Phenanthraquinone. GEORGE BARGER (T., 1918, **113**, 218—221).—3-Phenanthrol-4-aldehyde (A., 1916, i, 487) dissolved in pyridine reacts vigorously with hydrogen peroxide and potassium hydroxide to form morphol in excellent yield. The method is a modification of Dakin's process for converting *o*- and *p*-hydroxyaldehydes into dihydric phenols (P., 1909, **25**, 194). The oxidation of morphol to 3 : 4-*phenanthraquinone* may be achieved by means of dry silver oxide in ether.

For experimental details, see the original. J. C. W.

Preparation of Condensation Products from Aromatic Hydroxysulphonic Acids. BADISCHE ANILIN & SODA-FABRIK (D.R.-P., 301451; addition to 300567; from *Chem. Zentr.*, 1917, i, 787).—Phenolic mono- or di-alcohols are condensed with aromatic hydroxysulphonic acids, or with aromatic hydroxy-compounds followed by sulphonation of the products. For example, β-naphthol-6-sulphonic acid is condensed with *p*-homosaligenin, *p*-cresol with *p*-cresoldialcohol (the product has m. p. 215°), and 2-chloro-α-naphthol with *p*-homosaligenin and dihydroxyditolylmethane (m. p. 126°; from formaldehyde and *p*-cresol). J. C. W.

Condensation of Unsaturated Systems. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 932—939).—In addition to the matter referred to in A, 1917, i, 685, this paper contains a description of β-*phenyltrimethylene glycol* (α*γ-dihydroxycumene*),
$$CHPh(CH_2 \cdot OH)_2.$$
This is formed to the extent of 70%, together with some polymeric styrene, by the action of formaldehyde on styrene, $CHPh:CH_2 + H \cdot COH + H_2O = CHPh(CH_2 \cdot OH)_2$. It is a colourless oil, b. p. 145°/12 mm. When heated with acetic anhydride, it is converted quantitatively into the *acetate*, $CHPh(CH_2 \cdot OAc)_2$, b. p. 178°/12 mm.

Preparation of β-Naphthyl Benzoate. ANTHONY-HAMMOND CHEMICAL WORKS (U.S. Pat. 1254970).—One hundred and ten grams of β-naphthol are heated, and about 170 grams of benzoyl chloride are stirred in, drop by drop, any of the benzoyl chloride which is volatilised being condensed and returned, whilst the hydrogen chloride formed is allowed to escape. A. S.

Preparation of 6-Amino-3-sulphobenzoic Acid. FARBEN-
FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P., 296941; from
Chem. Zentr., 1917, i, 717).—Anthranilic acid is directly sulphon-
ated by means of ·chlorosulphonic acid in an indifferent solvent,
such as nitrobenzene, dichlorobenzene, or petroleum.   J. C. W.

m-**Nitrocinnamic Acid, Brominated in the Side Chain.**
S. REICH [with AGAMIRIAN, S. KOEHLER, J. GAJKOWSKI, and
(MLLE.) E. LUBECK] (*Arch. Sci. phys. nat.*, 1918, **45**, 191—216,
259—276).—A more detailed account of work already published
(compare A., 1914, i, 41). The following additional compounds
are described.

The acid described as β-bromo-*m*-nitrocinnamic acid, m. p.
177—179°, has m. p. 184°, and is really the *allo*-acid, giving a
methyl ester, m. p. 100—101°, and being converted by the action
of light into a stable *stereoisomeride*, m. p. 132°, giving a *methyl*
ester, m. p. 75—76°.

α-Bromo-*m*-nitro*allo*cinnamic acid when reduced in aqueous
barium hydroxide solution with ferrous sulphate yielded a *com-
pound*, brown needles, m. p. 206°. The *isomeride*, m. p. 217°,
when similarly reduced, yielded m-*aminophenylpropiolic acid*,
$NH_2 \cdot C_6H_4 \cdot C\!:\!C \cdot CO_2H$, m. p. 183°. On bromination, α-bromo-*m*-
nitro*allo*cinnamic acid yielded *ααβ-tribromo-β-m-nitrophenylpro-
pionic acid*, $NO_2 \cdot C_6H_4 \cdot CHBr \cdot CBr_2 \cdot CO_2H$, m. p. 157°, giving a
methyl ester, m. p. 107—110°. On warming with aqueous sodium
carbonate, this acid yielded *ββ-dibromo-*m-*nitrostyrene*, m. p. 58°,
which on bromination gave *αβββ-tetrabromo-*m-*nitrophenylethane*,
$NO_2 \cdot C_6H_4 \cdot CHBr \cdot CBr_3$, m. p. 87°. β-Bromo-*m*-nitrocinnamic acid
on bromination yielded *αββ-tribromo-β-*m-*nitrophenylpropionic
acid*, m. p. 165°, giving a *methyl* ester, m. p. 94—95°.

Attempts to esterify *m*-nitrophenylpropiolic acid by the action
of hydrogen chloride in the presence of methyl alcohol yielded
*methyl β-chloro-*m-*nitrocinnamate*, m. p. 113—114°.

The cuprous derivative of *m*-nitrophenylacetylene (*loc. cit.*), like
the derivatives of phenylacetylene and *o*-nitrophenylacetylene, is
oxidised by potassium ferricyanide, giving *dinitrophenyldi-
acetylene*, $NO_2 \cdot C_6H_4 \cdot C\!:\!C \cdot C\!:\!C \cdot C_6H_4 \cdot NO_2$, m. p. 149—150°, which
gives a *tetrabromo*-derivative, m. p. 160—161°. *m*-Nitrophenyl-
acetylene when brominated in chloroform solution gave a mixture
of cis-*αβ-dibromo-*m-*nitrostyrene*, m. p. 50—51°, and· its trans-
isomeride, m. p. 79°. These two isomerides on further bromina-
tion yielded *ααββ-tetrabromo-*m-*nitrophenylethane*,

$$NO_2 \cdot C_6H_4 \cdot CBr_2 \cdot CHBr_2,$$
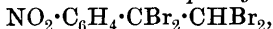
m. p. 96—97°. This compound or its isomeride (see above) when
treated in alcoholic solution with the theoretical quantity of
potassium hydroxide yielded *αββ-tribromo-*m-*nitrostyrene*, m. p.
90°.

cis-*αβ-Dibromo-*m-nitrocinnamic acid, m. p. 135—136°, gave a
methyl ester, m. p. 88°, and its *trans*-isomeride gave a *methyl*
ester, m. p. 118—119°.

ω-Bromo-*m*-nitrostyrene has m. p. 76—77°, and not 59° as previously given (*loc. cit.*), and during its formation from αβ-dibromo-*m*-nitrophenylpropionic acid there is produced at the same time some m-*nitrobenzoylacetic acid*,

$$NO_2 \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CO_2H,$$
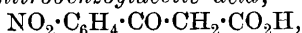
m. p. 150°. The bromonitrostyrene on bromination in chloroform solution yielded *tribromo*-m-*nitrophenylethane*,

$$NO_2 \cdot C_6H_4 \cdot CHBr \cdot CHBr_2,$$

m. p. 86—87°. W. G.

Preparation of Methyl *o*-Acetoxybenzoate. L. THORP (U.S Pat. 1255950).—Methyl salicylate is heated with acetic anhydride in the presence of alkali acetate for ten to twenty hours at 90—100°, then alcohol is added, followed by water until a turbidity is produced, and, after cooling, the ester is collected. A. S.

Normal Ammonium Salts of Organic Acids and their Substituted Derivatives. VII. LE ROY MCMASTER and LETA WRIGHT (*J. Amer. Chem. Soc.*, 1918, **40**, 683—693. Compare A., 1913, i, 248, 444; 1914, i, 481, 1122; 1915, i, 958; 1916, i, 707).— An account of several more *ammonium* salts, prepared by the action of ammonia gas on the acids in anhydrous solvents.

The 2-*hydroxy*-m-*toluate*, 4-*hydroxy*-m-*toluate*, and 3-*hydroxy*-p-*toluate* crystallise in cotton-like masses, and are non-hygroscopic and comparatively stable; the 2:4-*dihydroxybenzoate* is pale pink, and the 2:5-*dihydroxybenzoate* is white; the 2:4-*dinitrobenzoate* is insoluble in most organic media, except methyl alcohol; the *o*-, *m*-, and p-*nitrocinnamates* are not hygroscopic and only sparingly soluble in water; the α- and β-*naphthoates* begin to decompose at 50°. The *m*-nitrobenzenesulphonate; the m-*aminobenzene-sulphonate*, large, dark red plates; the α-*naphthylamine*-4-*sulphonate*, red and blue fluorescence in water; and the α-*naphthol*-4- and -5-*sulphonates*, unstable, brown powders, are described. The *benzilate* forms yellow granules; the oxanilate crystallises in slender needles, and the *phenylpropiolate* is a white powder.

J. C. W.

Preparation of Derivatives [Esters] of *iso*Valeric Acid. CHEMISCHE FABRIK VON FRIEDR. HEYDEN (Brit. Pat. 113983).— The esters are prepared by the interaction of hydroxy-fatty acids (for example, glycollic and lactic acids or acids containing an aryl group, such as mandelic acid) and *iso*valeric acid, halogen*iso*-valeric acids, especially α-bromo*iso*valeric acid, *iso*valeric anhydride, or *iso*valeryl chloride; or of *iso*valerates and the halogen fatty acids or their salts. They may be neutralised with inorganic or organic bases. The preparation of iso*valerylmandelic* [iso*valeryloxyphenyl-acetic*] *acid*, m. p. about 71°, both from *iso*valeryl chloride and from *iso*valeric acid, and of its calcium salt and its quinine salt,

m. p. 140°, of its α-bromo-derivative and of isovalerylglycollic [isovaleryloxyacetic] acid, m. p. 46—47°, both from glycollic acid and from sodium chloroacetate, is described.   A. S.

Preparation of an ω-Dihalogeno-*p*-toluoyl-*o*-benzoic Acid. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P., 297018; from *Chem. Zentr.*, 1917, i, 715—716).—When 2-*p*-toluoylbenzoic acid is treated with bromine at a high temperature, it is smoothly converted into 2-ω-*dibromo*-p-*toluoylbenzoic acid* (*4-dibromomethyl-2′-carboxybenzophenone*), a white powder, valuable as a source of anthraquinone derivatives, which changes into 4-*aldehydo-2′-carboxybenzophenone* [2-p-*aldehydobenzoylbenzoic acid*] on heating with dilute alkali hydroxides.   J. C. W.

The Phenylsuccinic Acid Series. VI. Racemisation Phenomena Observed during the Investigation of the Optically Active Phenyl- and Diphenyl-succinic Acids and their Derivatives. HENRY WREN (T., 1918, **113**, 210—218).— Since the esters of *r*-diphenylsuccinic acid are convertible into the esters of the *meso*-acid (this vol., i, 17), the same should be true of the optically active esters. The truth of this has been experimentally proved by the conversion of methyl and ethyl *l*-diphenylsuccinates into the *meso*-compounds by treatment with solutions of the appropriate sodium alkyloxides, and of ethyl *d*- and methyl *l*-diphenylsuccinates into *meso*-esters during partial hydrolysis.

It appears, therefore, that the considerable racemisation which occurs during the hydrolysis of these esters (A., 1915, i, 1061) is mainly due to rearrangement of the esters themselves, and not of the free acids. In this connexion, the more soluble *d*-phenylsuccinates have now been examined. The active methyl and ethyl esters are found to be rapidly and completely racemised by treatment with solutions of the alkyloxides, whilst the free *l*-phenylsuccinic acid is not appreciably affected. The portion of active ester which escapes hydrolysis when submitted to the action of insufficient potassium hydroxide dissolved in slightly diluted alcohol is also extensively racemised. Water has an influence on the extent of the racemisation, for the acid formed by complete hydrolysis with aqueous-alcoholic potassium hydroxide has a much higher rotation the greater the proportion of water in the agent.

The tendency in recent years is to explain racemisation in the case of such esters on the basis of keto-enol desmotropy (see Frankland, T., 1913, **103**, 725). No direct evidence of the usual kind has been obtained in the present case of the formation of sodium enolates, but, inasmuch as the strength of the alkali would have an influence on the extent of the enolisation, it is interesting to record that tetramethylammonium hydroxide causes even more complete racemisation of methyl *d*-phenylsuccinate than potassium hydroxide.   J. C. W.

Constitution and Spatial Formula of Quinic Acid.
HERMANN EMDE (*Apoth. Zeit.*, 1917, **32**, 601—602; from *Chem. Zentr.*, 1918, i, 208).—From the known physical properties of quinic acid, the author draws the conclusion that the substance is 1 : 3 : 4 : 5-tetrahydroxyhexahydrobenzoic acid. Quinide is the δ-lactone (I), and *l*-quinic acid is represented by the formula II.

(I.)   (II.)
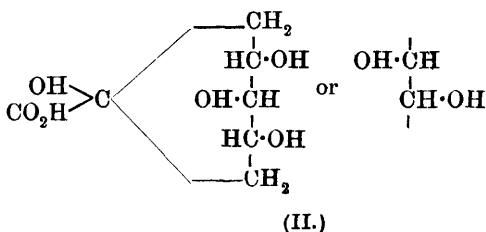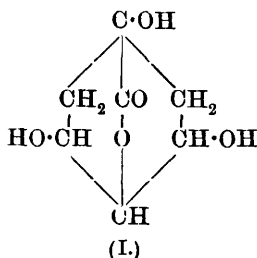
J. C. W.

Hydrosulphonic Derivatives of Citral. GIOVANNI ROMEO (*Gazzetta*, 1918, **48**, i, 45—52. Compare Tiemann and Lemme, A., 1899, i, 248).—With sodium hydrogen sulphite, citral forms the following compounds. (1) The normal compound,

$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CH(OH){\cdot}SO_3Na$,
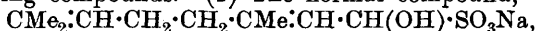
obtained in presence of a sufficient quantity of free acid, for instance, acetic acid, is crystalline and yields citral when treated with sodium hydroxide solution. (2) The stable dihydrosulphonic derivative, $C_9H_{17}(SO_3Na)_2{\cdot}CHO$, formed quantitatively when the normal compound is left for some hours in contact with sodium hydrogen sulphite solution maintained acid in reaction, is highly deliquescent, contains the aldehyde group unchanged, and is not decomposed by alkali hydroxide, even in the hot. Its constitution is represented by one of the four formulæ:

$SO_3Na{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}CMe(SO_3Na){\cdot}CH_2{\cdot}CHO$,
$CHMe_2{\cdot}CH(SO_3Na){\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH(SO_3Na){\cdot}CHO$,
$SO_3Na{\cdot}CMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}CH(SO_3Na){\cdot}CHO$,
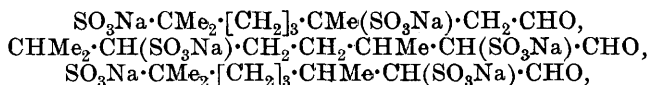
and $CHMe_2{\cdot}CH(SO_3Na){\cdot}CH_2{\cdot}CH_2{\cdot}CMe(SO_3Na)_2{\cdot}CHO$. (3) The labile dihydrosulphonic derivative, $C_9H_{17}(SO_3Na)_2{\cdot}CHO$, formed quantitatively when aqueous sodium hydrogen sulphite is shaken with citral and the alkali neutralised as it is formed, is crystalline and of neutral reaction, and is decomposed by alkali into citral and sodium hydrogen sulphite; by mineral or organic acids, it is slowly transformed into the stable modification. Its structure corresponds with one of the four formulæ given for the stable form. (4) Sodium citraldihydrosulphonate, $C_9H_{16}(SO_3Na){\cdot}CHO$, formed from citral and the labile dihydrosulphonate, is a solid, and immediately yields citral when treated in aqueous solution with potassium hydroxide. (5) Labile sodium citraltrihydrosulphonate, $C_{10}H_{19}O(SO_3Na)_3$, obtained from citral, sodium sulphite, and sodium hydrogen sulphite, is odourless, non-deliquescent, and of

neutral reaction, and is accompanied by a small proportion of (6), an isomeride stable towards potassium hydroxide.

<div align="right">T. H. P.</div>

Preparation of β-Aminoanthraquinone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255719).—β-Anthraquinonemonosulphonic acid is heated with ammonia and an aromatic nitro-compound, yielding β-aminoanthraquinone and the amino-compound corresponding with the nitro-compound used.

<div align="right">A. S.</div>

Crystallographic and Optical Characters of Amyrolin. HERMANN ROSE (*Jahrb. Min.*, 1918, 1—18).—Amyrolin, $C_{14}H_{12}O_3$ (von Soden and Rojahn, A., 1901, i, 159), has D^{18} 1·351 and m. p. 119—124°. The crystals are monoclinic, $a:b:c = 0·7583:1:1·1106$; $\beta = 76°55'$. The optical constants are given for wave-lengths 690·7 to 404·7 $\mu\mu$. For sodium light, $\alpha = 1·46447$, $\beta = 1·74798$, $\gamma = 1·94579$, $\gamma - \alpha = 0·48132$. The dispersion and double refraction are high, the latter being exceeded only by that of calomel.

<div align="right">L. J. S.</div>

Gossypol, the Toxic Principle of Cotton Seed. FRANK E. CARRUTH (*J. Amer. Chem. Soc.*, 1918, **40**, 647—663).—Gossypol is a colouring matter of phenolic nature occurring in glands in the seeds and in all parts of the cotton plant except the woody tissues. It is the toxic substance of cotton seed (compare A., 1917, i, 719). It may be precipitated as a compound with acetic acid or aniline by adding these agents to ethereal extracts of cotton seed. The first compound is decomposed by dissolving in ether, mixing with water, and distilling the solvent, when free gossypol separates on the surface, and the aniline salt is decomposed by hot alcoholic potassium hydroxide, the solution being then submitted to a current of steam and finally acidified.

Present analyses of gossypol, and molecular weight determinations, agree with the formula $C_{30}H_{28}O_9$ or $C_{30}H_{30}O_9$. The *compound* with acetic acid (1 mol.) corresponds with Marchlewski's gossypol (A., 1899, i, 821). A similar unimolecular *compound* with acetone, a *tetra-* or *penta-acetate* and *-benzoate*, a very sparingly soluble, orange-yellow *aniline* salt (2 mols. to $5NH_2Ph$?), and some metallic salts are described.

When heated at 186—190°, gossypol decomposes into a black mass, from which ether extracts a sparingly soluble, intensely yellow substance, m. p. 246—248°, termed B-*gossypol*. It is much less toxic than gossypol. Fusion with alkali hydroxide, followed by acidification in the presence of sodium hyposulphite (to prevent oxidation), gives a white product, C-*gossypol*. Cotton-seed meal, obtained by cooking the seeds for the oil, does not contain much gossypol as such, but D-gossypol (*loc. cit.*) instead. All four products behave alike in giving blood-red solutions in concentrated sulphuric acid and blue colorations when their alkaline solutions are exposed to the air. [See also *J. Soc. Chem. Ind.*, 319A.]

<div align="right">J. C. W.</div>

Analogues of Atropine and Homatropine. Louis F. WERNER (*J. Amer. Chem. Soc.*, 1918, **40**, 669—674).—When tropinone (I) is reduced by means of hydriodic acid, or electrolytically, it yields tropine, the tropate and mandelate of which are the well-known mydriatics atropine and homatropine. If reduced by means of sodium and alcohol, however, it gives ψ-tropine, the hydroxy-acid esters of which are not physiologically active. The alkaloid of the pomegranate, ψ-pelletierine (II), is a homologue of tropinone, and this also gives two isomerides on reduction.

$$CO\Big\langle \begin{array}{c} CH_2 \cdot CH{-}CH_2 \\ \ \ NMe \ \ \ \ | \\ CH_2 \cdot CH{-}CH_2 \end{array} \qquad CO\Big\langle \begin{array}{c} CH_2 \cdot CH{-}CH_2 \\ \ NMe \ \ CH_2 \\ CH_2 \cdot CH{-}CH_2 \end{array}$$

(I.)   (II.)
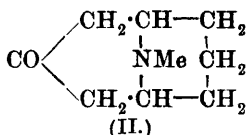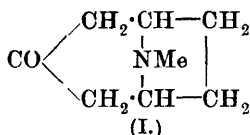
When treated with sodium and alcohol, it yields the alkamine, methylgranatoline (Ciamician and Silber, A., 1894, i, 154); the *hydrobromide* of the *tropate* of this, m. p. 220°, and the *hydrobromide* of the *mandelate* are powerful mydriatics. Reduction with hydriodic acid and zinc dust at 0° gives iso*methylgranatoline*, m. p. 65°; the *tropate hydrobromide*, m. p. 233°, and *mandelate hydrobromide*, m. p. 229°, of this are inactive. Compared with the tropines, therefore, the products formed by like methods of reduction give esters of opposite physiological effects.   J. C. W.

Preparation of Homologues of Emetine. FARBWERKE vorm. MEISTER, LUCIUS, & BRÜNING (D.R.-P., 301498; from *Chem. Zentr.*, 1918, i, 53).—Cephaeline is converted into its ethyl, propyl, and *benzyl* ethers. (Compare Karrer, A., 1916, i, 833, and Meader, *ibid.*, 834.)   J. C. W.

The supposed Formation of Ergotoxine Ethyl Ester from Ergotinine. A Correction. GEORGE BARGER and ARTHUR JAMES EWINS (T., 1918, **113**, 235—238).—The phosphate obtained by boiling ergotinine in alcoholic solution with phosphoric acid is the salt of ergotoxine itself and not of its ethyl ester, as was originally supposed (T., 1910, **97**, 284). From the results of Zeisel determinations, the authors are inclined to believe that ergotoxine and ergotinine contain one *N*-methyl group, but no methoxy-group.   J. C. W.

The Alkaloids of Ipecacuanha. III. FRANK LEE PYMAN (T., 1918, **113**, 222—234. Compare A., 1917, i, 410).—In the last communication it was shown that *O*-methylpsychotrine yields emetine and *iso*emetine on reduction. The formation of the latter isomeride was demonstrated by the isolation of its previously known benzoyl derivative; it is now confirmed by the actual separation of the base itself, some characteristic salts of which are described. On oxidation, *iso*emetine, like emetine, may be converted into *O*-methylpsychotrine or rubremetine, which shows

that the two bases are stereoisomerides. Equilibrium between them could not be established, however, by boiling with sodium and amyl alcohol. *iso*Emetine is rather less than half as toxic as emetine.

Psychotrine itself yields cephaeline and *iso*cephaeline on reduction, and, as might be expected, the latter may be converted into *iso*emetine by methylation. *iso*Emetine may be transformed under suitable conditions into *N*-methyl*iso*emetine, and this may also be formed by methylating *N*-methyl*iso*cephaeline (T., 1914, **107,** 1624).

N-Methyl*iso*emetine has also been completely methylated, the product being a mixture of a crystalline and an amorphous methiodide, apparently stereoisomerides, since they yield the same *N*-methyl*iso*emetine methine when the methohydroxides are heated. In the same way, emetine itself forms two *N*-methylemetine methiodides, which yield the same methine.

For details, the original should be consulted, where a chart showing the relationships between the ipecacuanha alkaloids, established experimentally by the author, will be found.   J. C. W.

Relative Stability of Cyclic Bases. VI. The Morpholine Ring. J. von BRAUN and Z. KÖHLER (*Ber.*, 1918, **51,** 255—265. Compare this vol., i, 185).—The authors have established the order of stability of a number of cyclic bases under the disruptive influence of cyanogen bromide and in the Hofmann reaction. It is now found that the morpholine system is to be placed along with tetrahydro*iso*quinoline and dihydro*iso*indole among the bases which are most easily ruptured by cyanogen bromide, and between these two in stability during the Hofmann reaction.

1-Methylmorpholine (I) (Knorr, A., 1898, i, 602) reacts very vigorously with cyanogen bromide diluted with ether, giving a crystalline precipitate of the hydrobromide of the base mixed with a trace of an undefined compound, $C_8H_{12}ON_5$, and a solution which contains an unstable oil (II). This condenses with piperidine to form β-*cyanomethylaminoethyl* β-1-*piperidinoethyl ether* (III), b. p. 170—175°/30 mm., which forms a *platinichloride*, stout, red, tablets, m. p. 166°, and a *picrate*, m. p. 139—140°. The main reactions are therefore represented by the scheme:

$$NMe\!\!<\!\!^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}\!\!>\!\!O \xrightarrow{BrCN} CN \cdot NMe \cdot C_2H_4 \cdot O \cdot CH_2 \cdot CH_2Br$$
$$\text{(I.)} \qquad\qquad\qquad\qquad \text{(II)}$$
$$\downarrow$$
$$CN \cdot NMe \cdot C_2H_4 \cdot O \cdot CH_2 \cdot CH_2 \cdot N\!:\!C_5H_{10}$$
$$\text{(III.)}$$
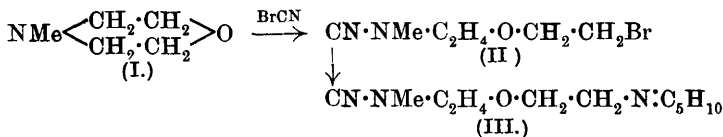
In order to compare the stability of the morpholine ring with the tetrahydro*iso*quinoline system under the conditions of the Hofmann reaction, a compound with a nitrogen atom common to both rings has been prepared. This is the *quaternary ammonium iodide*, $\begin{matrix}CH_2-CH_2\\C_6H_4 \cdot CH_2\end{matrix}\!\!>\!\!N\!\!<\!\!\begin{matrix}CH_2 \cdot CH_2\\CH_2 \cdot CH_2\end{matrix}\!\!>\!\!O$, which is obtained by mix-

ing tetrahydro*iso*quinoline, $\beta\beta'$-di-iodoethyl ether, and 10% aqueous sodium hydroxide. It is a pale yellow, crystalline salt, m. p. 214—215°, and the corresponding *platinichloride* has m. p. 230°. When the iodide is converted into the hydroxide and this is distilled under reduced pressure, the main product is 1-o-*vinylbenzyl-morpholine*, $CH_2{:}CH{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}O$, which boils at 138—142°/6 mm., with partial polymerisation, and forms a *hydro-chloride*, m. p. 211°, a *platinichloride*, red needles, m. p. 186°, a *picrate*, m. p. 164°, and a *methiodide*, m. p. 155—156°. The base combines with hydrogen bromide in concentrated solutions, forming an oily bromide (IV), which soon changes into the stable *quaternary bromide* (V), this having m. p. 213—215°, and yielding the corresponding red *platinichloride*, m. p. 220—223°. It may

$$CH_3{\cdot}CHBr{\cdot}C_6H_4{\cdot}CH_2{\cdot}N{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}O \;\longrightarrow$$
$$\text{(IV.)}$$

$$C_6H_4{<}^{CHMe}_{CH_2}{-}\underset{Br}{N}{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}O.$$
$$\text{(V.)}$$
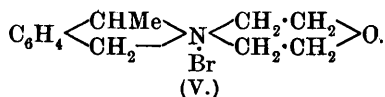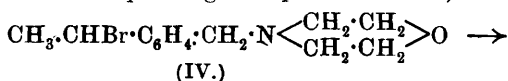
also be reduced to 1-o-*ethylbenzylmorpholine*, a viscous oil, b. p. 138—140°/11 mm. (*picrate*, m. p. 142°; *platinichloride*, m. p. 189°), which reacts with cyanogen bromide to form o-ethylbenzyl bromide (A., 1917, i, 259). These reactions of the base are sufficient evidence that it is 1-o-vinylbenzylmorpholine; in other words, that it is the tetrahydro*iso*quinoline ring, and not the morpholine ring, which is ruptured when the quaternary ammonium hydroxide is heated.

For a comparison between the morpholine and dihydro*iso*indole systems, morpholine, o-xylylene dibromide, and 10% sodium hydroxide are warmed together, the quaternary ammonium bromide so formed is converted into the hydroxide (VI) (*platinichloride*, m. p. 225°; *aurichloride*, m. p. 147°), and this is distilled. The chief product is 2-β-*vinyloxyethyldihydroisoindole* (VII), which has b. p. 176—180°/12 mm., and yields a *picrate*, m. p. 105°, and

$$C_6H_4{<}^{CH_2}_{CH_2}{>}N{<}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}\underset{OH}{>}O \;\longrightarrow\; C_6H_4{<}^{CH_2}_{CH_2}{>}N{\cdot}C_2H_4{\cdot}O{\cdot}CH{:}CH_2$$
$$\text{(VI.)} \qquad\qquad\qquad\qquad \text{(VII.)}$$
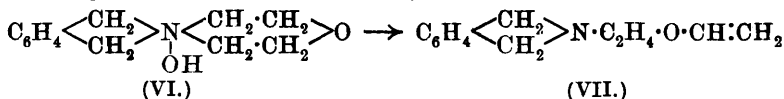
a *methiodide*, m. p. 129°. Consequently, the morpholine ring is the weaker in this case. J. C. W.

Bromoalkylated Aromatic Amines. II. J. von Braun, K. Heider, and E. Müller (*Ber.*, 1918, **51**, 273—282. Compare this vol., i, 107).—Some further reactions of methyl-β-bromoethyl-aniline are described, as well as the application of other secondary amines and ethylene dihaloids to the production of similar bromoalkylated bases.

When methyl-β-bromoethylaniline is heated with formaldehyde and hydrobromic acid, it yields *dimethyldi-β-bromoethyldiamino-*

diphenylmethane, $CH_2(C_6H_4\cdot NMe\cdot C_2H_4Br)_2$, which crystallises in colourless leaflets, m. p. 115—116°. If. hydrochloric acid is used, the bromine is replaced and *dimethyldi-β-chloroethyldiaminodiphenylmethane*, m. p. 97—98° (*picrate*, m. p. 147°) is formed.

With potassium phthalimide at 145—150°, the base reacts vigorously, forming *methyl-β-phthalimidoethylaniline*,

$$C_6H_4{<}^{CO}_{CO}{>}N\cdot C_2H_4\cdot NMePh,$$
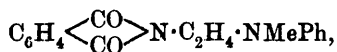
in canary-yellow, glistening leaflets, m. p. 109°; *methiodide*, m. p. 165°. The potassium salt of "saccharin" yields the corresponding *β-benzoicsulphinidoethylmethylaniline*,

$$C_6H_4{<}^{CO-}_{SO_2}{>}N\cdot C_2H_4\cdot NMePh,$$
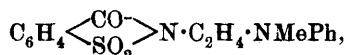
as a pale yellow, glistening mass, m. p. 115°, which forms an extremely bitter *methiodide*, m. p. 150°, and a p-*nitroso*-compound, a green powder, m. p. 190°, from which the p-*amino*-derivative, $C_6H_4{<}^{CO}_{SO_2}{>}N\cdot C_2H_4\cdot NMe\cdot C_6H_4\cdot NH_2$, may be obtained as a reddish-yellow powder, m. p. 111—112°. The "saccharin" derivative yields a flocculent diphenylmethane compound when heated with formaldehyde in the usual way. The hydrol obtained on oxidation with lead peroxide has a pure green colour in acid solutions, instead of the usual blue. To decide whether this difference is characteristic of the benzoicsulphinide group, a number of typical dyes (not described) have been prepared with this *tert.*-amine instead of a simple dialkylaniline, and in only one other case has an abnormally coloured product been obtained, namely, the compound related to methylene-blue, which is dark green.

Methylaniline reacts with *s*-chlorobromoethane under the conditions suitable for the production of methyl-β-bromoethylaniline to form a mixture of this with methyl-β-chloroethylaniline in almost equivalent quantities, having b. p. 116—120°/3 mm.

Ethylaniline and ethylene dibromide yield a mixture of diphenyldiethylethylenediamine, $C_2H_4(NEtPh)_2$, b. p. 223°/16 mm., and *β-bromodiethylaniline*, $NEtPh\cdot CH_2\cdot CH_2Br$. The latter is a pale yellow oil, b. p. 151—154°/15 mm., which forms a *picrate*, m. p. 95°, and resembles methyl-β-bromoethylaniline in all its activities. For example, it reacts with sodium to give *diphenyldiethyltetramethylenediamine*, $C_4H_8(NEtPh)_2$, b. p. 234—236°/12 mm.; *picrate*, m. p. 190°.

Methyl-o-toluidine and a large excess of ethylene dibromide, after heating for twenty-four hours, give a mixture of bases which are divided by distillation into (1) unchanged base, 20% of the weight of the base, (2) a fraction with b. p. 100—190°/6 mm., 40%, and (3) a fraction with b. p. about 200°/6 mm., 48%. The second fraction is freed from unchanged base by converting this into its nitroso-compound, and then yields on redistillation *methyl-β-bromoethyl-o-toluidine*, b. p. 118—120°/5 mm., which forms a *picrate*,

m. p. 90°, and reacts with trimethylamine to give the *quaternary bromide*, $C_6H_4Me\cdot NMe\cdot CH_2\cdot CH_2\cdot NMe_3Br$, glistening leaflets, m. p. 173—174°. The third fraction is mixed with trimethylamine to remove any bromoalkylated base as the foregoing salt, and then *di-o-tolyldimethylethylenediamine*, $C_2H_4(NMe\cdot C_6H_4Me)_2$, is re-covered as a hard mass, m. p. 46—47°, b. p. 199—201°/6 mm., which forms a *picrate*, m. p. 178°, and a *dibromide*, m. p. 88°.

Methyl-α-naphthylamine also yields a bromoalkylated base when heated with ethylene dibromide, but it decomposes on distillation. The parent substance is obtained as follows. The dimethyl-α-naph-thylamine of commerce is warmed with cyanogen bromide, which yields *α-naphthyltrimethylammonium bromide*, m. p. 160°, insoluble in ether, and *cyanomethyl-α-naphthylamine*, $C_{10}H_7\cdot NMe\cdot CN$, a yellow oil, b. p. 189—191°/5 mm., soluble in ether, and the latter is hydrolysed to methyl-α-naphthylamine by boiling with 20% hydro-chloric acid.

Tetrahydroquinoline and ethylene dibromide yield, chiefly, crys-talline s-1:1-*ditetrahydroquinolylethane*,

$$\begin{matrix} CH_2{-}CH_2 \\ CH_2\cdot C_6H_4 \end{matrix}{>}N\cdot CH_2.CH_2\cdot N{<}\begin{matrix} CH_2{-}CH_2 \\ C_6H_4\cdot CH_2 \end{matrix}.$$
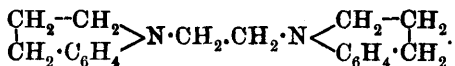
J. C. W.

Ethyl*iso*propylbarbituric Acid. L. THORP (U.S. Pat. 1255951). —Ethyl*iso*propylbarbituric acid, prepared by the usual methods, forms snow-white crystals (from water), m. p. 197—198°, has a faint, bitter taste, and is readily soluble in alcohol or ether. The acid and its alkali salts, which are readily soluble in water, possess marked hypnotic and sedative powers, and are relatively devoid of toxic action. A. S.

Compounds derived from Diallylbarbituric Acid and Alkaloids of the Morphine Series and Process of making same. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1255423, 1918; from *J. Soc. Chem. Ind.*, 1918, **37**, 193A. Com-pare A., 1917, i, 664).—The compound formed by diallylbarbituric acid and ethylmorphine is a white, crystalline substance, m. p. 285°. The compounds generally are easily soluble in hot water, methyl or ethyl alcohol, acetone, or ethyl acetate, but insoluble in light petroleum. H. M. D.

Preparation of Phenylethylbarbituric Acid. MARY RISING and JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1918, **40**, 723—730). —Some practical notes on the preparation of the necessary inter-mediate compounds and on the final stages in the synthesis of phenylethylbarbituric acid. This compound, which was introduced as a specific in cases of epilepsy under the name "luminal," is officially designated "phenylbarbital" in America, as veronal is termed "barbital." [See, further, *J. Soc. Chem. Ind.*, 322A.]

J. C. W.

Preparation of Nitrogenous Vat Dyes of the Anthracene Series. CHEMISCHE FABRIK GRIESHEIM ELEKTRON (D.R.-P., 301554; from *Chem. Zentr.*, 1918, i, 150).—The yellow vat dye obtained by the action of concentrated alcoholic alkali hydroxide on pyrazoleanthrone (A., 1913, i, 533) forms alkali salts which react with the usual alkylating agents. The alkyl derivatives so formed are much deeper in colour than the parent dye; for example, the *benzyl* compound is scarlet, and the *ethyl* derivative, Bordeaux-red.

J. C. W.

Halogenated Dyes of the Acridine Series. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255739).—A new acridine dye obtained by heating chloroformyl-*m*-phenylenediamine ($NH_2 : NH \cdot CHO : Cl = 1 : 3 : 6$) with *m*-phenylenedimethyl-diamine hydrochloride, is a brownish-black powder which dyes leather reddish-yellow. The patent covers derivatives of dyes of the general formula $NH_2 \cdot C_6H_3 \underset{CH}{\overset{N}{\diagdown\diagup}} C_6H_3 \cdot NR_1R_2$, in which R_1 and R_2 represent univalent substituents, including hydrogen, and one or more hydrogen atoms of the benzene nuclei have been displaced by halogen.

A. S.

Acridine Dyes of the Benzene-naphthalene Series. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (U.S. Pat. 1255740).—A new acridine dye of the formula:

$$\begin{matrix} (2)CH_3 \\ (3)(CH_3)_2N \end{matrix} > C_6H_2 \underset{CH}{\overset{N}{\diagdown\diagup}} C_{10}H_6$$
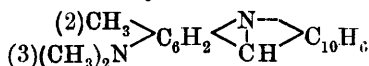
is a reddish-brown powder, which dyes leather in deep orange-yellow shades. The patent covers dyes of the general formula $R_2R_1N \cdot C_6H_3 \underset{CH}{\overset{N}{\diagdown\diagup}} C_{10}H_6$, obtained by heating a formyl derivative of β-naphthylamine with a salt of a *m*-diamine of the benzene series.

A. S.

Preparation of Condensation Products of Isatin and Ketones. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P., 301591; from *Chem. Zentr.*, 1918, i, 148—149).—Condensation products, of unexplained nature, are obtained by mixing acetophenone or its derivatives with isatin and ammonia solution. Acetophenone itself gives a pale yellow *product*, $C_{16}H_{12}O_3N$ [?], m. p. 152—153°; *p*-tolyl methyl ketone yields a white *product*, m. p. 165—167°; deoxybenzoin forms a *product*, m. p. 147°; and the *product* from 3-nitro-4-hydroxyacetophenone forms yellow crystals, m. p. 191°.

J. C. W.

Preparation of Mono-azo-dyes suitable for Pigment Manufacture. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 296991; from *Chem. Zentr.*, 1917, i, 718).—Diazotised 1-amino-anthraquinone is coupled with 1-benzoylamino-7-hydroxynaphth-

alene, or the substituted benzoylamino-analogues, in the presence of Turkey-red oil, or such substances, with or without a substrate. The 8-benzoylamino-β-naphthols employed are mostly colourless, crystalline compounds. The following are mentioned: 8-*benzoylamino-β-naphthol*, m. p. 208—209°; 8-*o-chlorobenzoylamino-β-naphthol*, m. p. 158—160°; 8-*p-chlorobenzoylamino-β-naphthol*, m. p. 230—231°; 8-*op-dichlorobenzoylamino-β-naphthol*, m. p. 186—187°; 8-*2′ : 6′-dichlorobenzoylamino-β-naphthol*, m. p. 230—232°; 8-*o-nitrobenzoylamino-β-naphthol*, m. p. 227—228°; 8-*m-nitrobenzoylamino-β-naphthol*, m. p. 204—205°; 8-*p-nitrobenzoylamino-β-naphthol*, m. p. 255—260° (decomp.). J. C. W.

Preparation of Acid Mono-azo-dyes for Wool. FARBEN-FABRIKEN VORM. F. BAYER & Co. (D.R.-P., 296964; from *Chem. Zentr.*, 1917, i, 717).—Good dyes which colour wool yellow to bluish-red or brown shades in acid baths are obtained by coupling pyrazolone-, methylketol-, α- or β-naphthol-, or 8-acylamino-α-naphthol-sulphonic acids with diazotised phenylenediamines of the type $NH_2 \cdot R'' \cdot NRR'$, where R = alkyl or aryl, R′ = an aromatic acyl group, such as Bz or $OMe \cdot C_6H_4 \cdot CO$, and R″ = the benzene nucleus or a homologue or substituted nucleus. The necessary bases are obtained by treating alkylated or arylated anilines with benzoyl chloride or substituted benzoyl chlorides, nitrating the products, and then reducing the nitro-compounds.

Thus, ethylaniline, after benzoylation, nitration, and reduction, yields *benzoylethyl-p-phenylenediamine*, $NH_2 \cdot C_6H_4 \cdot NEtBz$, m. p. 114°, and methylaniline gives *benzoylmethyl-p-phenylenediamine*, m. p. 143°. Benzoylethyl-*m*-toluidine yields *benzoylethyltolylene-2 : 5-diamine*, m. p. 140°; benzoylethyl-*p*-xylidine yields *benzoylethyl-p-xylylene-2 : 5-diamine*, $NH_2 \cdot C {\displaystyle <^{CH:CMe}_{CMe \cdot CH}>} C \cdot NEtBz$, m. p. 134°; benzoylmethyl-*o*-toluidine gives *benzoylmethyltolylene-2 : 4-diamine*, m. p. 167°; 2′-chlorobenzoylethylaniline gives *2′-chlorobenzoylethyl-p-phenylenediamine*, m. p. 135°; and 4-nitrodiphenylamine yields *benzoylphenyl-p-phenylenediamine*, m. p. 178°.

J. C. W.

Preparation of Yeast-nucleic Acid. EMIL J. BAUMANN (*Proc. Amer. Soc. Biol. Chem.*, 1917, xiv.-xv.; *J. Biol. Chem.*, 1918, **33**). —Fresh brewer's yeast is diluted with water and treated with sodium hydroxide solution (100 grams of alkali per kilo. of yeast) in the cold, which separates the nucleoprotein into protein and nucleic acid. Since nucleic acid is soluble in dilute acetic acid, the solution is now partly neutralised with hydrochloric acid and then made acid with acetic acid. The precipitated proteins are removed by filtration and the nucleic acid in the filtrate precipitated by the addition of 5% magnesium sulphate solution and enough hydrochloric acid to cause the separation of the flocculent precipitate. The yield of dry mono-magnesium nucleate is 4 to 7½ grams per kilo. of yeast H. W. B.

Nucleic Acid of the Lymph Corpuscle. R. NAKASAKO (*A. C. James Res. Lab., Bull.*, 1917, No. 3; from *Physiol. Abstr.*, 1918, **3**, 4—5).—The nucleic acid was prepared from lymph glands by a modification of Kossel's method. It closely resembles the thymus acid, and to it the author assigns the formula $C_{41}H_{55-64}O_{25}N_{14}P_4$. Amongst the products of hydrolysis, xanthine, hypoxanthine, guanine, adenine, thymine, and a compound containing either of the groups $CH_3 \cdot CO \cdot C$ and $CH_3 \cdot CH(OH) \cdot C$ were identified. The existence of a carbohydrate is uncertain.

W. G.

Effect of Potassium Bromate on Enzyme Action. I. S. FALK and C.-E. A. WINSLOW (*J. Biol. Chem.*, 1918, **33**, 453—462). —Potassium bromate exerts a slight stimulating action on trypsin and pancreatin when it is present in concentrations of 1 part in 100,000 to 1 part in 250,000. With higher concentrations, the proteolytic action is depressed. H. W. B.

Action of Ammonium Compounds on Ptyalin. ELBERT W. ROCKWOOD (*Proc. Amer. Soc. Biol. Chem.*, 1917, ix–x; *J. Biol. Chem.*, 1918, **33**).—Ammonium salts of inorganic and organic acids increase the activity of ptyalin. In general, the ammonium salts of the strong acids have a greater activating effect than those of the weak acids. Ammonium oxalate is an exception, having little or no action. H. W. B.

The Action of Acids on Ricinus Lipase and the Reaction of the Substratum. G. KITA (*J. Chem. Ind., Tokyo*, 1918, **21**, 1—4).—Green and Hoyer have shown that acids have a powerful activating influence on the lipase of castor beans, and that the activated lipase exerts its specific activity in neutral media. Further, lipase which has been rendered active by treatment with acids and thoroughly washed has a more powerful action in faintly acid media than in neutral. The author has found that the activated lipase, which is extremely unstable in presence of acids, becomes comparatively far more permanent in presence of the oil to be hydrolysed. Armstrong overlooked this fact, and considered that the acid played some other part than the liberation of the zymogen, because the quantity of acid which is most favourable to fat hydrolysis was capable under the same conditions of destroying the lipase of de-fatted castor beans. The author considers that, although the activated lipase is again rendered inactive by acids, the simultaneous presence of fat is capable of exerting a protective action on the lipase in the hydrolysis of fats. J. F. B.

The Action of Aldehydes on Urease. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **85**, 358—364).—Aldehydes inhibit the action of urease. The cyanohydrin of acetaldehyde, however (but not that of benzaldehyde) accelerates the action. S. B. S.

Preparation of Aromatic Stibinic Acids. CHEMISCHE FABRIK VON HEYDEN, AKT.-GES. (D.R.-P., 296940; with 261825 and 269255, an addition to 254421; from *Chem. Zentr.*, 1917, i, 715. Compare A., 1913, i, 416, 1122; 1914, i, 217).—Nitro-derivatives of aromatic stibinic acids are prepared by treating diazo-tised nitroamines with antimonites or antimonious acid, in acid or neutral solutions, at low temperatures. Antimony trioxide dissolved in such an acid as tartaric acid is recommended, and copper powder is often useful as a catalyst. *2-Nitro-* and *2:4-dinitro-phenylstibinic acids* are brown powders which explode on heating. 3-Nitro-*p*-anilinoarsinic acid yields *2-nitro-4-arsinophenylstibinic acid*, $AsO_3H_2 \cdot C_6H_3(NO_2) \cdot SbO_3H_2$, which is a similar brown powder.

J. C. W.

Physiological Chemistry.

The Oxygen and Carbon Dioxide Tension in the Blood of the Pulmonary Artery and the Measurement of the Minute Volume of the Heart. L. S. FRIDRICIA (*Biochem. Zeitsch.*, 1918, **85**, 307—357).—The method of measurement employed by the author is described in detail. It is based on the use of a spirometer constructed by Krogh on the principle of the aeroplethysmograph. It was found that the tensions of oxygen and carbon dioxide in pulmonary blood are not constant in the same individual when in a state of rest. The average values for three persons were 40·7, 44·5, and 35·1 mm. for oxygen and 45·2, 46·3, and 45·2 mm. for carbon dioxide. There are wider variations, therefore, in the oxygen than in the carbon dioxide tensions. During muscular work (200 kg./m. per minute), the ratios of the tensions to the tensions found for the same individual when at rest were for oxygen 35·2 : 44·5, and for carbon dioxide 55·2 : 46·3. The minute volume of the heart was estimated by the methods of Krogh and Lindhard and of Fick, and the two were found to give results which were satisfactorily concordant.   S. B. S.

Comparison of the Dextrose and Cholesterol Content of the Blood. F. H. McCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1918, **33**, 387—389).—The amounts of dextrose and of cholesterol in the blood in various diseases do not show any kind of parallelism. The association of hyperglycæmia and hypercholesterolæmia in diabetes (Bloor, Joslin, and Hornor, A., 1916, i, 776) is therefore probably due to an indirect physiological relationship.   H. W. B.

Fatty Acids in Human Blood in Normal and Pathological Conditions. FRANK A. CSONKA (*J. Biol. Chem.*, 1918, **33**, 401—409. Compare A., 1916, ii, 349).—The method

previously described for the estimation of fatty acids in fæces (Gephart and Csonka, A., 1915, ii, 74) can be applied in the case of blood, using 5 c.c. of oxalated blood, and the author's saponification and extraction flask (*loc. cit.*). For the estimation of the unsaturated fatty acids, about 100 c.c. of blood are extracted with alcohol and ether, and the extract saponified by the Gephart and Csonka method. The mixed fatty acids are converted into their lead soaps, which are then extracted with ether, which dissolves the lead soaps of the unsaturated fatty acids. The free acids are liberated from the soaps by hydrochloric acid, and, after weighing, the iodine numbers are determined according to Hübl.

The blood of normal individuals contains about 0·14 gram of unsaturated fatty acids per 100 c.c., with an average iodine number of 87·5. The iodine number varies from 76 to 105, thus indicating the presence, in addition to oleic acid, of other both higher and lower unsaturated fatty acids in small amounts. In normal human blood, about one-half of the total fatty acids are unsaturated. In pathological conditions, there is generally a higher proportion of unsaturated fatty acids with higher iodine values, especially in cases where the hæmoglobin content of the blood is low. In such cases, the smaller number of red corpuscles present in the blood reduces the amount of unsaturated fatty acid which can be utilised for metabolic purposes, and this results in an accumulation of unsaturated fatty acids in the blood (compare Bloor, A., 1916, i, 450).   H. W. B.

Adsorption Phenomena in Coagulation. G. H. A. CLOWES (*Proc. Amer. Soc. Biol. Chem.*, 1917, xx; *J. Biol. Chem.*, 1918, **33**).—The author has determined the effect on the coagulation of blood of the addition of precipitated or colloidal barium sulphate, calcium oxalate, etc., which adsorb prothrombin. The adsorption is proportional to the degree of dispersion of the adsorbent and depends also on the presence of unsaturated lipoids like kephalin. Apparently the physical quality and speed of formation of the blood clot depend on the degree of dispersion of the reacting colloids and on their initial and final concentrations.   H. W. B.

Relation between Phosphorus Metabolism and the Secretion of Milk-fat. EDWARD B. MEIGS and N. R. BLATHERWICK (*Proc. Amer. Soc. Biol. Chem.*, 1917, iv—v; *J. Biol. Chem.*, 1918, **33**).—Experiments on cows are described in which the distribution of phosphorus in the blood is determined before entering and after leaving the mammary gland. When the cow is disturbed by the operative procedure, the lipoid phosphorus in the blood remains unaltered, but when the cow is quiet, a diminution in the lipoid phosphorus occurs during the passage of the blood through the active gland. In all cases, an increase in the inorganic phosphate in the blood coming from the gland is observed.

The authors consider that the results show that the precursor

in the blood of both milk fat and milk phosphorus is either lecithin or a related compound. The ratio phosphorus : fat in lecithin is about 1 : 18, whereas it is about 1 : 50 in milk. Hence relatively more phosphorus is supplied to the gland than is required for the milk, and the excess is returned to the blood as inorganic phosphate. H. W. B.

Metabolism of α-Carbamido*iso***butylacetic Acid.** ALICE ROHDE (*Proc. Amer. Soc. Biol. Chem.*, 1917, xii; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 344).—The intravenous injection of α-carbamido*iso*butylacetic acid in saline solution into a cat is followed by the elimination of a considerable proportion of the acid in the urine. The acid is identified by the method previously described in the case of phenylalanine–carbamido-acid (*loc. cit.*).
H. W. B.

Endogenous Uric Acid Metabolism. HOWARD B. LEWIS, MAX S. DUNN, and E. A. DOISY (*Proc. Amer. Soc. Biol. Chem.*, 1917, xv—xvi; *J. Biol. Chem.*, 1918, **33**).—The authors describe the influence of the ingestion of proteins and various protein derivatives on the hourly elimination of uric acid in a subject on a purine-free low protein diet. Protein (egg-white, cheese) causes a slight rise, beginning the second hour after the meal and increasing to a maximum at the fourth hour. Ingestion of equivalent amounts of nitrogen in the form of glycine or alanine results in a sharp rise in the second hour, followed by a prompt return to the normal level. Administration of a second portion of glycine following the return to normal causes a like increase in the uric acid excretion. Aspartic and glutamic acids produce eliminations of uric acid of even greater magnitude. Neither urea nor ammonium chloride administered in amounts comparable to the amino-acids has any influence on the output of uric acid. The authors draw the conclusion that the rise in the excretion of uric acid following ingestion of protein food is not due mainly to the work of the digestive glands, but to stimulation of the cellular mechanism by the amino-acids liberated in the digestion of the protein. Creatinine excretion was not affected in any of the experiments. H. W. B.

Role of some Inorganic Elements in Nutrition. LAFAYETTE B. MENDEL and THOMAS B. OSBORNE (*Proc. Amer. Soc. Biol. Chem.*, 1917, iii; *J. Biol. Chem.*, 1918, **33**).—The essential factors of a successful dietary having now been ascertained, it has become possible to prepare rations in which the individual ions are excluded except for the unavoidable small amounts present in the products used to supply the water-soluble vitamine or found as impurities in the other ingredients of the food. Experiments with such diets demonstrate that calcium and phosphorus are needed in considerable amounts, for with only a trace of either of these elements in the diet, rats fail to grow and sooner or later decline.

On diets in which one of the elements magnesium, sodium, potassium, or chlorine are absent, growth continues at the normal rate. When both sodium and potassium are absent, growth does not occur.   H. W. B.

Formation of Structures Resembling Organic Growths by Electrolytic Action in Metals. R. S. LILLIE (*Biol. Bull.*, 1917, **33**, 135—186; from *Physiol. Abstr.*, 1918, **3**, 7—8).—A study of the conditions under which filaments, formed of ferricyanides of iron, zinc, copper, etc., are produced in mixtures of albumin and potassium ferrocyanide. Only those metals the ferricyanides of which form semipermeable membranes exhibit the phenomenon. The author suggests that in organic growth the essential structural condition is possibly the presence of semipermeable, and hence electrically polarised, partitions separating the living substance from its medium, and at which the process of electrolysis may take place.   W. G.

Differences in the Swelling of the Plasma Colloids as a Cause of the Invagination of the Gastrula and generally of the Curving and Folding of Layers of Cells. JOSEF SPEK (*Koll. Chem. Beihefte*, 1918, **9**, 259—399).—A paper, mainly of biological interest, in which an attempt is made to show that changes in the geometrical form of certain tissues are due to differences in the extent to which the colloidal constituents of the cells are swollen by the absorption of water. The degree of swelling is appreciably affected by the electrolytes present, and the results of some observations on the swelling of fibrin under the influence of solutions of acids and salts are recorded. These show that for salt concentrations which fall within the physiological range, the effect of the presence of acids is to increase considerably the degree of swelling of the plasma colloids.   H. M. D.

Autolysis. H. C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1917, xi; *J. Biol. Chem.*, 1918, **33**).—The autolysis of nervous tissue, like muscle and gland tissues, is accelerated by acids and inhibited by alkalis. Striated muscle autolyses more slowly than either cardiac or involuntary muscle. The accelerating action of inorganic hydrosols on the autolysis of liver described by Ascoli and Izar (A., 1909, ii, 501) is not confirmed.   H. W. B.

Conjugation of Hippuric Acid. E. LACKNER, A. LEVINSON, and WITHROW MORSE (*Proc. Amer. Soc. Biol. Chem.*, 1917, xvi—xviii; *J. Biol. Chem.*, 1918, **33**).—After fatty degeneration of the liver has been produced in dogs by the subcutaneous injection of hydrazine, ingestion of sodium benzoate causes a diminished output of hippuric acid compared to that observed in the normal animal. Apparently the kidney is not affected by the hydrazine injection, and therefore the authors draw the conclusion that, normally, conjugation of hippuric acid occurs in the liver. These

results are confirmed by the following clinical observations. In normal children, ingestion of sodium benzoate produces an increased elimination of hippuric acid. A case of a child with diseased liver is described in which administration of sodium benzoate did not have any effect on the output of hippuric acid.

<div align="right">H. W. B.</div>

Creatine Content of Skeletal Muscle in Degeneration following Denervation. E. P. CATHCART, P. S. HENDERSON, and D. NOËL PATON (*J. Physiol.*, 1918, **52**, 70—74).—Up to the eleventh day after section of the nerve there is no distinct change, but after the fifteenth day, when the reaction of degeneration is well established, there is a steady and progressive decrease in the creatine content of muscle, becoming very pronounced (30—60%) between the third and fourth weeks.

<div align="right">G. B.</div>

Guanidine Content of Muscle in Tetania Parathyreopriva. PEARL S. HENDERSON (*J. Physiol.*, 1918, **52**, 1—5).—Removal of the parathyroids causes a fall in the total and in the free guanidine of muscle and a rise in the creatine content corresponding fairly closely with the fall in free guanidine. The fall in total guanidine is, however, so great that it may be correlated with the increase in blood and urine (compare Burns, A., 1916, i, 617).

<div align="right">G. B.</div>

Cell Penetration by Acids. IV. Penetration of Phosphoric Acid. W. J. CROZIER (*J. Biol. Chem.*, 1918, **33**, 463—470. Compare A., 1916, i, 694).—With mantle tissue of *Chromodoris*, the coagulating action of phosphoric acid is so pronounced that a relatively high concentration must be employed before there is marked acceleration in the speed with which the quantity of acid sufficient to react with the indicator is forced to diffuse into the tissue. The actual speed of protoplasmic penetration by phosphoric acid is probably much greater than its apparent magnitude.

<div align="right">H. W. B.</div>

Catalase Content of Ascaris suum, with a Suggestion as to its Rôle in Protecting Parasites against the Digestive Enzymes of their Hosts. THOMAS BYRD MAGATH (*J. Biol. Chem.*, 1918, **33**, 395—400).—The relative amounts of catalase contained in two or more tissues are estimated by measuring the volumes of oxygen evolved when equal weights of the tissues are placed in contact with excessive quantities of hydrogen peroxide. The apparatus employed is similar to that used for the estimation of urea by the hypobromite method; hydrogen peroxide is placed in the bottle together with a crucible containing the weighed tissue. The bottle is connected with a measuring burette and levelling tube filled with water. After the crucible has been upset, the oxygen evolved is readily measured and corrected for normal temperature and pressure.

The whole worm yields 15 c.c. of oxygen per gram, the body

wall 13 c.c., the body fluid 7 c.c., and the visceral organs 26 c.c. per gram. Whilst these amounts are small as compared with those obtained from free living animals, it is pointed out that if the catalase in the respective reproductive organs be taken as the unit, then the body wall of *Ascaris* contains three times as much catalase as the leg muscles of the frog. It is probable, therefore, that there is more than enough catalase in the body wall of this worm for its metabolic and locomotory functions, and it is possible that the excess is used to liberate oxygen for protecting the parasite against the digestive enzymes of its host (see Burge, A., 1915, i, 614).

H. W. B.

Food Fishes. Analysis of Twenty Common Food Fishes with Especial Reference to a Seasonal Variation in Composition. ERNEST D. CLARK and LLOYD H. ALMY (*J. Biol. Chem.*, 1918, **33**, 483—498).—The authors have analysed the edible portions of various fishes at different periods of time. In the case of the shad, the spawning period is about two months, during which time the fish appear in the rivers in April and ascend to freshwater, returning to the sea in June. The amount of fat in the edible portion of the fish diminishes from 14·4% before spawning to 2·95% afterwards. The shad, like the salmon, does not feed during the spawning migration, and doubtless some of the fat is consumed in the tissues to furnish the energy necessary for ascending the rivers, and the remainder is transferred to the roe and milt.

In most fishes, the fat content varies inversely as the water content, the proportion of fat-free solids remaining constant. The fish oils are fairly uniform, the constants being D_{25}^{25} 0·9220, n_D^{30} 1·4750, iodine number 110—130, and saponification number 180—190. The amounts of water-soluble nitrogen and coagulable nitrogen are also fairly constant for the same kind of fish taken at different times, whilst the amounts of these substances may be widely different for different species of fish.   H. W. B.

The Biochemistry of Certain Conditions of Oedema. I. Blood and Serum. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **85**, 365—405).—The investigations refer to certain cases of " oedema disease" observed chiefly in prisoners of war. The chief results were the following: Diminution in blood, especially in the plasma of fatty acids and lipoid phosphorus; hypoglycæmia, increase in acetone substances, residual nitrogen, ammonia, cholesterol, and acid-soluble phosphorus; small increase in sodium chloride. Diminution of iron and potassium; moderate hydræmia, but, with the exception of lymphocytosis, no marked abnormality in the formal elements of the blood, and other characters. The author discusses the clinical bearings of the results.   S. B. S.

The Part Played by an " Accessory Factor" in the Production of Experimental Rickets. EDWARD MELLANBY (*Proc. Physiol. Soc.*, 1918, xi—xii; *J. Physiol.*, **52**).—Two diets,

(1) milk, rice, oatmeal, and sodium chloride, (2) milk and bread, produce rickets in puppies in the course of three to four months if the milk is kept below 200 c.c. per day. Rickets was prevented by extracts of meat, malt, and yeast, by butter, margarine, and cod-liver oil, but not by protein of meat, casein, linseed oil, or 10 grams of yeast per day. Hence it would appear that rickets is due to the lack of an accessory factor in the diet.　　　　　　　　G. B.

Degradation of Aliphatic Acids in the Animal Body.　EMIL LENK (*Münch. Med. Woch.*, 1917, **64**, 1460; from *Chem. Zentr.*, 1918, i, 121).—The author has shown that acetoacetic acid may be oxidised to acetic acid by heating with acetic acid and permanganate (A., 1917, ii, 399), and believes that a similar degradation of the acid by the attack of oxidising agents on the ethylene linking (of the enolic modification) may proceed in the body. Other facts indicate that acetic acid may be formed in the body as the result of reduction, so the degradation of fatty acids, which is so complete that only traces of the higher members are ever found in normal urine, may be due to both processes.　　J. C. W.

Elimination of Taurine administered to Man.　CARL L. A. SCHMIDT, EDWARD VON ADELUNG, and THOMAS WATSON (*J. Biol. Chem.*, 1918, **33**, 501—503).—The administration of from 3 to 10 grams of taurine subcutaneously, intravenously, or by the mouth is followed by an increased elimination of neutral sulphur in the urine. From 59 to 86% of the taurine sulphur is thus recoverable from the urine. Large doses of taurine administered to rabbits or to human subjects do not appear to produce any toxic effects.　　　　　　　　　　　　　　　　H. W. B.

The Character of the Toxic Action of Suprarenine [Adrenaline].　OSCAR LOEW (*Biochem. Zeitsch.*, 1918, **85**, 295—306).—When in the form of its salts in a neutral solution, adrenaline has only a very slightly toxic action. The free base, however, and its first red oxidation product is extremely toxic, and this action can be readily demonstrated on the nucleus of *Spirogyra*. The author ascribes the toxicity to the lability of the hydrogen ions in the molecule, which is specially marked in alkaline solution.
　　　　　　　　　　　　　　　　　　　　　　　　　S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

Nitrogen Content of Bacterial Cells. I. Method.
HAROLD C. BRADLEY, and M. STARR NICHOLS (*J. Biol. Chem.*, 1918, **33**, 525—529).—The bacterium is grown on a solid medium and the culture then transferred by a glass spatula to a tared

cover-slip and dried at 37° in a desiccator to constant weight. The nitrogen is subsequently estimated by Folin's micro-method.

Employing quantities of about 5 mg. of dry bacteria for analysis, *B. diphtheriae* are found to contain about 8·4, and *B. hoffmanni* 9·6 per cent. of nitrogen.   H. W. B.

The Bacterial Metabolism of Sulphur. II. Formation of Hydrogen Sulphide from certain Sulphur Compounds by Yeast-like Fungi. FRED W. TANNER (*J. Amer. Chem. Soc.*, 1918, **40**, 663—669).—The growth of some thirty varieties of budding fungi, mainly yeast species, has been studied in culture media containing peptone, cystine, sodium thiosulphate, sulphate, and sulphite, potassium thiocyanate, thiocarbamide, sodium phenolsulphonate and taurocholate, or sulphur itself. All of them were found to produce hydrogen sulphide from cystine, but only eleven developed it from peptone; twenty-two varieties gave very positive results with the thiosulphate, and distinct lead paper reactions when grown with the sulphite, whilst ten reduced even the sulphate; about two-thirds produced hydrogen sulphide from free sulphur; sodium taurocholate was reduced by two varieties only, and the phenolsulphonate by *Mycoderma lactis* only, although growth was quite good on this substrate. *M. lactis* has the largest all-round reducing power.   J. C. W.

Bactericidal Properties conferred on the Blood by Intravenous Injection of Diaminoacridine Sulphate. C. H. BROWNING and R. GALBRANSEN (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 136—144).—Attention is directed to the fact that certain acridine derivatives, unlike most other antiseptics, have a stronger bactericidal action in the presence than in the absence of serum, and, furthermore, that the toxic action increases progressively with time. Some experiments show that when diaminoacridine sulphate is injected into rabbits, their sera become bactericidal to *Staphylococcus aureus* and *B. coli*, even after heating at 56°.   S. B. S.

Enzyme Formation. HANS EULER (*Biochem. Zeitsch.*, 1918, **85**, 406—417).—Attention is directed to the fact that the formation of a ferment (invertase) in developing yeast is not necessarily parallel with the rate of growth. A series of experiments was carried out with culture media containing, in addition to sucrose and the necessary inorganic salts, the following substances as sources of nitrogen: glycine, glycine + cystine, glycine + tyrosine, asparagine, alanine, and yeast water. There was no marked difference in the rate of growth with different amino-acids, but it was less than that in yeast water. In yeast water, the rate of formation of invertase was greater than in presence of pure aminoacids, but here again there was no marked difference in the action of the individual acids.   S. B. S.

Volutin and its Chemical Composition. M. A. VAN HERWERDEN (*Folia Microbiologica. Nederl. Tydschr. voor Mikrobiologie*, 1917, **5**, pp. 12; from *Chem. Zentr.*, 1918, i, 216).—If

organisms like *Ustilago maydis, Torula monosa,* lactose yeast, or *Saccharomyces cerevisiae* are cultivated on media which are free from phosphates, they do not develop volutin, but this immediately appears in the cells if the cultures are transferred to a phosphate mixture. A nucleic acid derivative is also extracted from ordinary cultures when the isolation of volutin is aimed at, but the same procedure fails to remove nucleic acid compounds from a culture which contains no volutin. The conclusion is therefore drawn that volutin itself is a nucleic acid derivative. The living cell, even if volutin is absent, contains zymase, catalase, and nuclease, the latter being able to liberate phosphoric acid from nucleic acids. The stimulation of fermentation by volutin is therefore probably due to the steady production of small quantities of phosphoric acid from it.

J. C. W.

The Plasmotype-Volumetric Method and its Applicability to the Measurement of the Osmotic Value of Living Plant Cells. KARL HÖFLER (*Ber. Deut. bot. Ges.*, 1917, **35**, 706—726).— In the original experiments of de Vries, a comparison was made between the concentrations of the solutions of different substances which were just capable of producing perceptible plasmolysis in the immersed plant cells. When more concentrated external solutions are employed, plasmolysis takes place until the issuing water has reduced the volume of the cell sap to such an extent that the internal and external solutions are isotonic. By the use of suitable plant cells, it is possible to measure the volume of the protoplast when equilibrium has been reached by means of a measuring microscope, and from the relation between this volume and the volume of the cell, the osmotic concentration of the original cell sap may be calculated. The results obtained in a series of experiments in which the concentration of the external (sucrose) solution was varied show a close agreement. It seems possible that the method may be applied in the investigation of the deviations of the osmotic concentration of cells from the average or normal values.

H. M. D.

The Physiologically Active Constituents of certain Philippine Medicinal Plants. II. HARVEY C. BRILL and ALBERT H. WELLS (*Philippine J. Sci.*, 1917, **12**, [A], 167—198. Compare A., 1907, ii, 500).—A continuation of the examination of medicinal plants occurring in the Philippine Islands. A summary of previous knowledge and of native applications of the plants is given in each case.

Lophopetalum toxicum, Loher (N.O., *Celastraceae*), is a tree from the bark of which the natives obtain a juice with which to poison their weapons, care being taken by them not to leave the extract in contact with sour substances. A yield of 0·8% of a very toxic saponin, crystallising in clusters of needles, m. p. 183°, was obtained from the fresh bast fibre.

The bark of *Erythrophloeum densiflorum,* Merrill (*Leguminosae*),

contains tannins but no alkaloids, the substance erythrophleine found in *E. guineense* being absent from this species.

Quisqualis indica, Linn. (*Combretaceae*), gives fruits with yellow kernels which have been a popular anthelmintic and laxative in the East for some centuries. The seeds contain a yellow oil, possessing purgative but not anthelmintic properties, a sugar, 3·87% of potassium sulphate, and a gum which shows many alkaloidal reactions.

Tylophora brevipes, F.-Vill. (*Asclepidaceae*), is valued by the Filipinos as an emetic and expectorant, a decoction of the roots being used. The plant is closely related to *T. asthmatica*, well known in India for its resemblance in properties to ipecacuanha, and it contains the same alkaloid, tylophorine (Hooper, A., 1891, 1267).

Toddalia asiatica, Kurz (*Rutaceae*), has been widely known for centuries on account of the febrifugal and anti-diarrhœal properties of its roots, being mentioned in old pharmacopœias as "*Radix indica lopeziana*," or *tinct. toddalia*, especially in India. Its active principle is berberine.

Lunasia amara, Blanco (*Rutaceae*), the native name for which signifies "bitterness itself," provides a close-grained wood which is so hard that the Negritos often use it for the tips of their arrows, but not to poison the weapons, as is wrongly supposed. The juice of the seeds is used against the bite of poisonous animals, and the bark and seeds are held to be useful in gastralgia. The bark and leaves contain about 0·6% of intensely bitter alkaloidal substances of moderate physiological activity, wholly or chiefly consisting of lunasine, already reported by Boorsma. Prior to Boorsma's work in 1900, it appears that all accounts of *Lunasia* were founded on specimens sent to European museums, which were really *Lophopetalum toxicum*.

Rourea erecta, Merrill (*Connaraceae*), is a vine, the roots and berries of which are used by native quack doctors for a variety of ailments. The berries, even old, dry specimens, contain an active principle which is very toxic to carnivora but not to herbivora.

Hymenodictyon excelsum (*Rubiaceae*) of the Philippines contains no alkaloid, but differs from Indian varieties in that the active febrifuge is not æsculin, but β-methylæsculetin (compare Gibson and Simonsen, this vol., i, 151). The product isolated had m. p. 203°, and gave an *acetyl* compound, rhombic prisms and plates, m. p. 177°, and agreed with Schmidt's compound from *Gelsemium sempervivens* (A., 1899, i, 72).   J. C. W.

Organic Chemistry.

The Oxidation Products of Paraffin. MAXIMILIAN BERGMANN (*Zeitsch. angew. Chem.*, 1918, **31**, 69—70).—White, refined paraffin wax of Galician origin, m. p. 52°, was oxidised by blowing a fairly rapid current of air through it at 130—135° for fifteen to eighteen days. The soft brown product of the oxidation had an acid value of 132 and gave strongly frothing soap solutions with alkali hydroxides. On distilling the crude mass, decomposition set in at about 300°, with formation of formic, acetic, and *n*-butyric acids. The separation of the fatty acids from the neutral substances was therefore effected by forming the barium soaps and extracting the dried precipitate with ether. The isolated fatty acids had an acid value of 200 and were fractionated by distillation under 100 mm. pressure; about one-half distilled between 230° and 270° and one-third between 270° and 310°. The latter fraction showed an iodine value of 4; it was converted into the lithium soap, which was dried and extracted with ether and light petroleum, to separate the last traces of unsaponifiable matter. The liberated fatty acid was converted into the ethyl ester, m. p. 55°, after recrystallisation from alcohol. The purified acid had m. p. 80·1°. It was thus characterised as *lignoceric acid*, and proved to be identical with the lignoceric acid prepared from earth-nut oil. The fraction boiling between 230° and 270° had an iodine value of 5; by extraction of its lithium soap, a neutral substance was extracted crystallising from methyl alcohol in leaflets, m. p. 48°. The liberated fatty acids were separated by crystallisation from acetic acid into two substances: one crystallising in shining needles, m. p. 53·7°, acid value 299·4, corresponding with the formula $C_{11}H_{22}O_2$, which gave strongly frothing soap solutions with alkali hydroxides; and the other, separated from the mother liquors by precipitation as the lithium soap, which had m. p. 210—212°, having a composition corresponding with $C_{16}H_{32}O_2$, m. p. 38·4°, and acid value 217·05. The latter acid might be an *iso*palmitic acid. J. F. B.

Solubility of Hydrocarbons (Paraffin, Aromatic, Naphthene and Olefine) in Liquid Sulphur Dioxide. R. J. MOORE, J. C. MORELL, and G. EGLOFF (*Met. and Chem. Eng.*, 1918, **18**, 396—402).—The solubility of individual hydrocarbons, of binary mixtures, and of a ternary mixture, of paraffins, aromatic hydrocarbons, and naphthenes has been studied. Solubilities were determined by bringing the liquid sulphur dioxide and the hydrocarbons together in a burette immersed in a freezing mixture of ice, salt, and calcium chloride at temperatures down to −18°. Benzene, toluene, xylene, mesitylene, and olefines were miscible with the solvent in all proportions. Paraffins up to decane were practically insoluble. Naphthenes showed a solubility limited

at $-18°$, which was more pronounced at $-4·5°$. There is evidence of the formation of a molecular compound with the solvent. The separation of the mixed hydrocarbons of different types by liquid sulphur dioxide is limited by the partition of the hydrocarbons between the two phases, but by attention to the relative proportions, some approximation to a quantitative separation is possible, generally where the constituent to be extracted is in small proportion. Aromatic hydrocarbons and olefines, together or separate, can be separated from paraffins and naphthenes. Naphthenes can be separated from paraffins. Over methods of sulphonation and nitration, this method has the advantage of permitting recovery of both hydrocarbon and solvent and also of avoiding the production of undesirable by-products .   H. J. H.

Action of Concentrated Sulphuric Acid on Olefines, with Particular Reference to the Refining of Petroleum Distillates. BENJAMIN T. BROOKS and IRWIN HUMPHREY (*J. Amer Chem. Soc.*, 1918, **40**, 822—856).—The data at present available as to the behaviour of various olefines with sulphuric acid are scanty and somewhat conflicting, and as a preliminary to an investigation of the action of sulphuric acid on olefines as applied in the refinery of petroleum distillates, the authors have examined the effect of sulphuric acid on synthetic unsaturated hydrocarbons of definite purity and known constitution.

The chief results of the action of sulphuric acid on olefines are polymerisation and the formation of secondary and tertiary alcohols and of alkyl hydrogen and dialkyl sulphates. Contrary to the general assumption in the petroleum industry, no mono-olefine hydrocarbon was found to yield a "tar" when treated with the acid at 15°. In the aliphatic series, the tendency to form alkyl sulphates and alcohols decreases with increasing molecular weight above the amylenes and hexenes, at which a maximum is observed (compare Michael and Brunel, A., 1909, i, 197; 1912, i, 821). The introduction of strongly electronegative groups into ethylene causes a decrease in the reactivity towards sulphuric acid, as is demonstrated by the relative inertness of fumaric and cinnamic acids and of dichloroethylene towards the acid, whilst, inversely, $\beta\gamma$-dimethyl-Δ^β-butylene, in which each of the hydrogen atoms is replaced by the electro-positive methyl radicle, is more reactive than the isomeric α-hexene; a similar consideration also explains the greater reactivity of amylene, butylene, and propylene as compared with ethylene. This point of view, however, fails to explain the relative stability of the olefines of still higher molecular weight, nor does it appear to throw much light on the difference between the behaviour of γ-ethyl-Δ^β-pentene, which yields 72% of the alcohol and 12% of polymerides and of the structurally similar β-methyl-Δ^β-undecene, which gives 97% polymerides and a trace of alcohol, or on the fact that vinylacetic acid yields crotonic acid, whereas the isomeric α-methylacrylic acid gives a polymerisation product; styrene, cinnamyl alcohol, eugenol, *iso*eugenol, and safrole also

undergo vigorous polymerisation to hard, resinous substances. With increasing molecular weight, the tendency towards polymerisation develops, and duodecene is found to undergo almost quantitative conversion into a dipolymeride; the polymerides generally are open-chain hydrocarbons still containing at least one double bond, and are naturally much more stable than the parent olefines towards sulphuric acid; the result of this is that when petroleum is refined with sulphuric acid, the viscous polymerides are not found in the used acid, but remain to a large extent in the layer of refined oil. The common assumption that the more viscous petroleum oils, for example, of the lubricating oil type, consist exclusively of naphthenes and polynaphthenes is therefore not above suspicion, and the presence of a considerable percentage of polymerised olefines is probable, not only from the fact that the oils have been treated with sulphuric acid, but from the definite iodine value of such oils.

When the simpler alkylenes are dissolved in cold 85% sulphuric acid at below 15°, clear amber-coloured solutions are obtained which on treatment with ice give an immediate oily precipitate consisting mainly of the corresponding alcohol, whilst the aqueous acid solution, containing a considerable proportion of the original hydrocarbon as the alkyl hydrogen sulphate, fails to yield any appreciable further deposit of oil even during several days; the alkyl hydrogen sulphates, therefore, are not readily hydrolysed under such conditions; from these results and the fact that pure sulphuric acid alone does not convert hexenes into the alcohols, it is probable that the formation of alcohols by the action of diluted sulphuric acid on alkylenes may be independent of any intermediate occurrence of sulphuric esters of the known type and may be attributed to the intermediate formation of an easily hydrolysable orthosulphate analogous to sulphuric acid mono-hydrate, H_4SO_5, or of an easily hydratable additive compound of the olefine with sulphuric acid corresponding with the zinc chloride or aluminium chloride additive compounds (compare Gangloff and Henderson, A., 1916, i, 593; 1917, i, 533).

In the course of the investigation, the following olefinic hydro-carbons were examined in a high degree of purity: β-methyl-Δ^a-butylene, b. p. 33—35°; β-methyl-Δ^a-pentene, b. p. 64—66°; Δ^a-n-hexene, b. p. 60·5—61·5° (earlier descriptions are inaccurate), the constitution of which is demonstrated by its conversion through the chlorohydrin into the corresponding glycol; ε-methyl-Δ^a-hexene (*iso*heptene), $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$, b. p. 85—86°, D_{15}^{15} 0·7160; Δ^γ-n-heptene, b. p. 93—95°, D_{20}^{20} 0·7020, which combines with benzenesulphonic acid at the ordinary temperature, yielding an undistillable heptyl benzenesulphonate, D_{20}^{20} 0·979; γ-ethyl-Δ^β-pentene, b. p. 97—98°; βγ-dimethyl-Δ^β-butene (tetramethyl-ethylene), b. p. 73—74°, D_{20}^{20} 0·7075; Δ^a-octene, b. p. 122—124°, D 0·7240 (dipolymeride, b. p. 195—230°), although it is not certain that this may not in reality be the Δ^β-isomeride; ζ-*methyl*-Δ^a-*heptene* (iso*octene*), $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH{:}CH_2$, b. p.

111—112°, D_4^{20} ʊ 7125, n_D^{20} 1·3986 (*dipolymeride*, b. p. 112—114°/ 16 mm., D 0·798); *β-methyl-Δ^β-undecene*, $CMe_2:CH·C_8H_{17}$, b. p. 210—211·5°/752 mm., D_4^{20} 0·7590, n_D^{20} 1·4270. For the synthetic production of Δ^α-ethylenic hydrocarbons, the interaction of allyl bromide and a magnesium alkyl bromide was found convenient; the formation of unsaturated hydrocarbons by the action of heat on the higher alcohols is found to be greatly facilitated by the addition of a little iodine. In the preparation of ζ-methyl-Δ^α-heptene by the former method, using magnesium *iso*amyl bromide and allyl bromide, a *decane*, b. p. 156·5—157·5°, n_D^{20} 1·4006, D_{20}^{20} 0·7270, probably of the constitution $C_2H_4(CH_2·CHMe_2)_2$, was obtained as a by-product.   D. F. T.

Preparation of Glycols. CHEMICAL DEVELOPMENT Co. (U.S. Pat. 1259757).—A mixture of olefine dichlorides prepared from oil-gas is converted into the corresponding glycols (ethylene, propylene, and butylene glycols) by heating with water and calcium carbonate under pressure.   A. S.

Preparation of Glycols and Glycol Derivatives. CHEMICAL DEVELOPMENT Co. (U.S. Pat. 1259758).—A mixture of olefine dihaloids is heated under pressure with the calcium salt of a weak acid, for example, calcium acetate. (See also preceding abstract.)   A. S.

Lecithin. II. Preparation of Pure Lecithin; Composition and Stability of Lecithin–Cadmium Chloride. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1918, **34**, 175—186. Compare this vol., i, 98).—Pure lecithin may be obtained from egg yolk by extracting with acetone and alcohol, and then redissolving the concentrated extract several times in dry acetone, which effects a separation from lipoids insoluble in acetone. The oil is then extracted with a large volume of hot alcohol, the alcoholic extract cooled to 0°, the solution decanted from the egg-fat, concentrated, and the lipoid mixture precipitated with cadmium chloride. The lecithin-cadmium chloride is recrystallised from a mixture of ethyl acetate and 80% alcohol until free from amino-nitrogen (kephalin), and is then decomposed by ammonium carbonate according to Bergell's method (A., 1900, i, 621). The resulting lecithin does not contain any amino-nitrogen.   H. W. B.

Preparation of Acetic Acid from Acetaldehyde. H. DREYFUS (Brit. Pat. 108459. Compare this vol., i, 251).—The oxidation of acetaldehyde to acetic acid by means of air or oxygen, either in presence or absence of contact substances, is most complete if effected at 150—250°, preferably 150—200°. Copper (clippings, gauze, powder) is a more efficient catalyst than platinum. Chromium compounds are also very efficient, and other suitable catalysts are copper oxide, iron, uranium oxide, vanadium oxide, and cerium oxide.   A. S.

Preparation of Acetic Anhydride and Polymerised or Non-polymerised Acetaldehyde. Société Chimique des Usines du Rhône (Brit. Pat. 110906).—Ethylidene diacetate is decomposed almost quantitatively into acetic anhydride and paraldehyde by heating it in a vacuum with an acid or acid salt as catalyst, for example, with 2% of sulphuric acid (D 1·84) at 70—80°/100 mm. A. S.

The State of Potassium Oleate and of Oleic Acid in Solution in Dry Alcohol. Mary Evelyn Laing (T., 1918, 113, 435—444).—Measurements have been made of the changes in the boiling point of ethyl alcohol which are produced by the addition of gradually increasing quantities of potassium oleate. The molecular weight calculated from the results is independent of the concentration and slightly less than that corresponding with the formula. In moist alcohol similar results were obtained.

From the measured values of the electrical conductivity at 40° and 60°, it is inferred that the ionisation increases from about 3% in 1N- to about 30% in 0·03N-solution.

The conductivity of solutions of oleic acid in ethyl alcohol has also been measured at 60° over a wide range of concentration. The degree of ionisation is very small, and the results afford evidence that the ionisation varies with dilution in accordance with the requirements of the law of mass action.

The conductivity of potassium oleate in alcohol is diminished by the addition of oleic acid. This suggests the formation of a complex compound, and evidence in support of this hypothesis is afforded by boiling point observations on solutions containing mixtures of the salt and acid.

The observations on potassium oleate agree with those previously made by Krafft on the salts of other fatty acids and show that these substances behave as normal electrolytes in alcohol, although in aqueous solution they afford examples of colloidal electrolytes. H. M. D.

Preparation of a Crystalline Ester of the Di-iodide of Ricinstearolic Acid. J. D. Riedel (D.R.-P., 303052, 1914 ; from *Chem. Zentr.*, 1918, i, 498).—Ethyl ricinstearolate di-iodide, colourless needles, m. p. 31°, can be obtained by esterifying the di-iodide of ricinstearolic acid or by the addition of iodine to ethyl ricinstearolate. D. F. T.

Ethyl Thioacetoacetate [Ethyl Acetoacetate Sulphide], Ethyl α-Chloroacetoacetate, and a New Formation of Oxalic Acid. Fr. von Konek-Norwall (*Ber.*, 1918, 51, 391—398).—When antipyrine is treated with sulphur chlorides, it yields a mono- and di-sulphide (A., 1911, i, 505), but the parent ethyl acetoacetate only forms a monosulphide, S(CHAc·CO₂Et)₂ (A., 1885, 1200). With the hope of obtaining a disulphide, some pure ethyl α-chloroacetoacetate was purchased about six years ago to

be treated with sulphur, but it was recently found that the specimen had gradually deposited crystals of oxalic acid dihydrate.

J. C. W.

Photochemical Reactions in Aqueous Solution. II. ALFRED BENRATH (*J. pr. Chem.*, 1917, [ii], **96**, 190—201. Compare A., 1912, ii, 881; 1911, ii, 681).—When mixed with iron alum in aqueous solution in a sealed glass tube exposed to sunlight, tartaric acid undergoes photochemical oxidation with formation of dihydroxytartaric acid, which is not isolable, but rapidly decomposes in part into glyoxalcarboxylic acid, $CHO \cdot CO \cdot CO_2H$, and carbon dioxide (compare Ciamician and Silber, A., 1913, ii, 545; Seekamp, A., 1894, i, 323); the formation of this acid is proved by its isolation as its di-phenylhydrazone and by the relative proportion of the reagents which participate in the change. Part of the dihydroxytartaric acid, however, undergoes further oxidation to carbon dioxide, probably by way of mesoxalic acid, and carbon dioxide is also formed as the final product in the further oxidation of the glyoxalcarboxylic acid, probably through tartronic acid and mesoxalic acid; small quantities of glyoxal, glyoxylic acid, and formaldehyde can also be detected, but these are regarded as by-products, the first being produced by the partial elimination of carbon dioxide from glyoxalcarboxylic acid, whilst the last two form minor successive oxidation products of mesoxalic acid. The correctness of these views is confirmed by photochemical experiments with the postulated intermediate products.

Citric acid in aqueous solution, with the addition of iron alum and a little sulphuric acid, becomes oxidised in sunlight during the course of a few days with formation of carbon dioxide, acetone, and a little formaldehyde. In a similar oxidation of glycollic acid, formaldehyde and glyoxylic acid can be detected, whilst malic acid is relatively resistant, and the only identified products were acetaldehyde and formaldehyde.

When a mixture of formic acid with ethyl alcohol, or acetic acid with methyl alcohol, in a sealed tube is exposed to light for twelve months, the resulting liquid can be shown to contain the corresponding ester, together with formaldehyde and acetaldehyde in addition to unchanged ingredients, whilst with acetic acid and ethyl alcohol only ethyl acetate and acetaldehyde are formed; the conclusion is drawn that the resulting ester undergoes partial decomposition into the two aldehydes. In a similar manner, a mixture of formic and malic acids produces carbon dioxide, formaldehyde, and acetaldehyde, and the same substances are formed in the interaction of oxalic acid and acetone; a mixture of formic acid and citric acid yields carbon dioxide, formaldehyde, and acetone, and a mixture of formic acid and acetone gives rise to formaldehyde.

D. F. T.

Formaldehyde in Air. D. G. J. BOLTEN (*Pharm. Weekblad*, 1918, **55**, 60—61).—The evolution of formaldehyde vapour from formalin for disinfecting purposes can be brought about by the action of quicklime. The process has the advantage that there

is no oxidation of the formaldehyde. In the permanganate method, 2% of the formaldehyde is lost through oxidation.   A. J. W.

Preparation of Dialdehydesulphoxylic Acids. ARTHUR BINZ (D.R.-P., 303478, 1916; from *Chem. Zentr.*, 1918, i, 498).— *Diformaldehydesulphoxylic acid*, $S(O \cdot CH_2 \cdot OH)_2$, can be obtained from a formaldehydesulphoxylate, formaldehyde solution, and alcoholic hydrogen chloride; similarly, *dibenzaldehydesulphoxylic acid* is obtainable from benzaldehydesulphoxylate. The analogous *formaldehydebenzaldehydesulphoxylic acid*, $OH \cdot CH_2 \cdot O \cdot S \cdot O \cdot CHPh \cdot OH$, reacts with p-*toluidine*, yielding the *substance*
$$C_6H_4Me \cdot NH \cdot CH_2 \cdot O \cdot S \cdot O \cdot CHPh \cdot OH.$$ D. F. T.

Action of Sodium Acetylide on Aldehydes and Ketones. K. HESS and H. MUNDERLOH (*Ber.*, 1918, **51**, 377—384).— Primary, secondary, and tertiary alcohols of the acetylene series have been prepared by the action of sodium phenylacetylide, $CPh{:}CNa$, on formaldehyde, other aldehydes and ketones, respectively (compare Nef, 1899, and Moureu, 1901—1902). The behaviour of unsubstituted sodium acetylide, $CH{:}CNa$, has therefore been examined. This is found to react in the above manner to a very minor extent. Generally speaking, most of the acetylene escapes as gas, the sodium uniting with the carbonylic compound and inducing polymerisation and intermolecular condensations.

Acetone reacts vigorously, even at $-15°$, about 64% of the acetylide decomposing into gas. After decomposing the product with dilute sulphuric acid, extracting with ether, and fractionating the oil thus isolated, the following compounds were obtained : (1) γ-*Methylbutinen-γ-ol*, $OH \cdot CMe_2 \cdot C{:}CH$, a volatile, mobile, pungent-smelling oil, b. p. 102—103°/745 mm., 25°/12 mm., yield 2·8%; this gives a white precipitate with mercuric chloride which yields trimethylketol, identified by its semicarbazone (Schmidt and Austin, A., 1902, i, 2), on boiling with hydrochloric acid. (II.) Mesityl oxide, sufficient in quantity to identify as its semicarbazone. (III.) Diacetone alcohol, b. p. 67—68°/19 mm., yield about 1·3%. (IV.) *iso*Phorone, b. p. 86—87°/11 mm., yield 36·9%; this has been identified by its semicarbazone and also reduced by sodium amalgam to the *pinacone*,

$$CH_2\!\!<\!\!{}^{CMe_2 \cdot CH_2}_{CMe{=}CH}\!\!>\!\!C\underset{}{\diagup}\!\!\overset{OH\quad OH}{\underline{}}\!\!\overset{}{\diagdown}C\!\!<\!\!{}^{CH_2 \cdot CMe_2}_{CH{=}CMe}\!\!>\!\!CH_2,$$
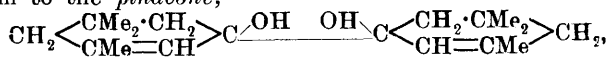
m. p. 162°.   (V.) "*iso*Phorone-acetylene" (annexed formula), a viscous, pungent oil, b. p. 115—116°/12 mm., yield 2·2%.

$$\begin{array}{c} CMe \\ \diagup\diagdown \\ CH_2 \quad CH \\ | \qquad | \\ CMe_2 \quad C(OH) \cdot C{:}CH \\ \diagdown\diagup \\ CH_2 \end{array}$$
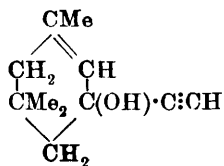
Reaction with acetaldehyde is still more vigorous. The only recognisable product is a minute quantity of *butinen-γ-ol*,
$$OH \cdot CHMe \cdot C{:}CH,$$
which is a limpid, lachrymatory oil, b. p. 105—106°/742 mm. Benzaldehyde gives as the chief product benzyl benzoate.
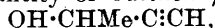
Notes on the preparation of sodium acetylide are given.   J. C. W.

The Influence of Certain Substances on Starch Solutions, and the Action of Amylase of the Saliva. J. TEMMINEK GROLL (*Arch. néerland. physiol.*, 1918, **2**, 319—336).—Reversible transformations of starch into an erythroamylose, giving a red or violet colour with iodine-potassium iodide solution, take place when starch solutions are treated with methyl, ethyl, or octyl alcohol, ethyl ether, and chloroform in various concentrations. If sodium cholate or saponin is added in addition to these substances, the transformation into erythroamylose becomes irreversible. This action of cholate and saponin is ascribed to a surface-tension effect. The salivary amylase, under the influence of cholate and saponin, acts on starch solutions, producing reducing substances which colour the iodine solution red or brown. After some minutes, however, the starchy substance is reconstituted, the reducing substances disappear, and the solution gives a blue colour with iodine. After a further long period, the starchy substance disappears, and products are produced which do not colour iodine. It is suggested that it is possible, by simply lowering surface tension, to obtain catalytic decomposition of a colloidal substrate (soluble starch).

S. B. S.

Wood Pulp. CARL G. SCHWALBE (*Zeitsch. angew. Chem.*, 1918, **31**, 50—56; 57—60).—A description of the different classes of wood pulp and of its chemical properties. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

Two Forms of Glycine. K. GEORGE FALK and KANEMATSU SUGIURA (*J. Biol. Chem.*, 1918, **34**, 29—36. Compare Fischer, A., 1905, i, 863).—Glycine crystallises from water in plates and from dilute alcohol in needles. After drying at 100°, the plate form begins to decompose on heating at 212°, whilst the needle form remains unchanged until a temperature of 220° to 230° is reached. There are also differences in the behaviour of the two forms towards nitrous acid and towards bromine; in one experiment, each molecule of the needle form absorbed 2 atoms of bromine, whilst the plate form absorbed 1 atom. Similar experiments with the corresponding two forms of alanine showed similar although less marked differences. Possible structural formulæ are suggested to account for the observed differences between the two forms of glycine and alanine respectively.

H. W. B.

Preparation of Formamide. ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 793—796).—Formamide purified by fractional distillation has m. p. 2·25° (English and Turner, Trans., 1914, **105**, 1656, give 2·0—2·2°). [See also *J. Soc. Chem. Ind.*, July.]

D. F. T.

Rotatory Powers of the Amides of Active α-Hydroxy-acids. C. S. HUDSON (*J. Amer. Chem. Soc.*, 1918, **40**, 813—817).—The sign of the optical activity of the amides of *d*-gluconic acid, *d*-galactonic acid, *l*-mannonic acid, *d*-gulonic acid, *l*-arabonic acid, *l*-ribonic acid, and *d*-xylonic acid (Weerman, A., 1915, i, 387;

1917, i, 546), as also of the amides of d-α-glucoheptonic acid and of l-rhamnonic acid in aqueous solution, is in agreement with the general rule that the dextrorotatory amides have the α-hydroxyl group below the asymmetric α-carbon atom, whilst with the lævorotatory amides it is above, the constitutions being represented by ordinary plane formulæ placed horizontally with the amide group to the right (compare Levene, A., 1916, ii, 3; Levene and Meyer, A., 1916, ii, 545; 1917, i, 631; Hudson, A., 1910, i, 220; 1917, i, 318). This result is in accord with the structure of d-tartaric acid as decided by Fischer (A., 1896, i, 525) and with the direction of the optical activity of tartramic acid (Weerman, *loc. cit.*) and of the amides of tartaric acid (Frankland and Slator, T., 1903, **83**, 1354; Frankland and Twiss, T., 1906, **89**, 1853). The optical activities of the amide of l-malic acid (Walden, A., 1896, i, 139) and of the amide of d-glyceric acid (Frankland and Wharton, T., 1901, **79**, 266) are also found to obey this rule, and the agreement serves to confirm the structures attributed to these acids (Freudenberg, A., 1914, i, 924). The amide derived from amygdalin mandelic acid has a lævorotation, and on this evidence the α-hydroxyl group in this mandelic acid is believed to occupy a position above the asymmetric atom when the structure is formulated in the manner described.   D. F. T.

Hydrazides and Azides of Organic Acids. XXXIII. The Action of Hydrazine and Nitrous Acid on Di- and Triglycollamic Esters. Theodor Curtius and Otto Hofmann (*J. pr. Chem.*, 1917, [ii], **96**, 202—235).—Iminodiacetic acid (diglycollamic acid) can be obtained conveniently by heating chloroacetic acid with the additive compound of zinc chloride and ammonia, esterifying the resulting mixture of acids by heating with alcoholic hydrogen chloride and then separating the ethyl esters of aminoacetic acid, iminodiacetic acid, and nitrilotriacetic acid by distillation under reduced pressure; another very convenient process is based on that of Jongkees (A., 1908, i, 959) for the preparation of iminodiacetonitrile, which by treatment with alcoholic hydrogen chloride can be converted directly into ethyl iminodiacetate (compare Dubsky and Gränacher, this vol., i, 188); if iminodiacetonitrile is suspended in ether and submitted to the action of nitrous fumes, nitrosoiminodiacetonitrile is obtained, m. p. 43° (Bailey and Snyder, A., 1915, i, 389, give m. p. 38°).

Ethyl iminodiacetate, $D^{16.5}$ 1·0851, b. p. 133°/11 mm., reacts with hydrazine hydrate at the ordinary temperature, yielding *iminodiacetic hydrazide*, $NH(CH_2 \cdot CO \cdot NH \cdot NH_2)_2$, leaflets or tablets, m. p. 133°, which forms a *trihydrochloride*, a *triacetyl* derivative, m. p. 204—205° (decomp.), and slowly reacts with ketones and aldehydes, giving condensation products; acetone, salicylaldehyde, and benzaldehyde respectively, giving rise to the *compounds*
$$NH(CH_2 \cdot CO \cdot NH \cdot N{:}CMe_2)_2,$$
small rods, m. p. 176°; $NH(CH_2 \cdot CO \cdot NH \cdot N{:}CH \cdot C_6H_4 \cdot OH)_2$, small rods, m. p. 201—202° (with decomp.); and
$$NH(CH_2 \cdot CO \cdot NH \cdot N{:}CHPh)_2,$$
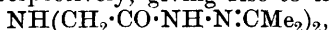
q^{*}
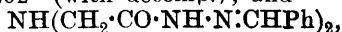
small rods, m. p. 201—202° (decomp.). If the condensation is allowed to proceed in the presence of mineral acid, the products are the corresponding salts of these substances, and always contain water of crystallisation, thus

$$2NH(CH_2 \cdot CO \cdot NH \cdot N\dot:CH \cdot C_6H_4 \cdot OH)_2, H_2SO_4, H_2O,$$
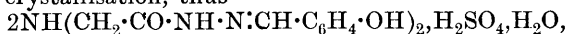
pale yellow solid, m. p. 190° (decomp.);

$$2NH(CH_2 \cdot CO \cdot NH \cdot N\dot:CHPh)_2, H_2SO_4, 6H_2O,$$
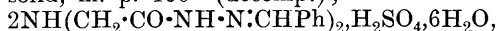
m. p. 173—175°; $NH(CH_2 \cdot CO \cdot NH \cdot N\dot:CHPh)_2, HCl, 2H_2O$, needles, m. p. 249—250°; $NH(CH_2 \cdot CO \cdot NH \cdot N\dot:CHPh)_2, HNO_3, 2H_2O$, m. p. 202—203°; $NH(CH_2 \cdot CO \cdot NH \cdot N\dot:CHPh)_2, HNO_2, 2H_2O$, m. p. indistinct near 135°; it was not found possible to convert the last, by dehydration, into a nitroso-compound.

On treatment with nitrous gases, ethyl iminodiglycollate is converted into *ethyl nitrosoiminodiacetate*, $NO \cdot N(CH_2 \cdot CO_2Et)_2$, a viscous, yellow oil, b. p. 175°/14 mm., which is also obtainable from ethyl iminodiacetate hydrochloride and sodium nitrite in the presence of water, and from nitrosoiminodiacetonitrile by the action of alcohol and hydrogen chloride. Ethyl nitrosoiminodiacetate reacts with alcoholic ammonia solution, giving nitrosoiminodiacetamide, $NO \cdot N(CH_2 \cdot CO \cdot NH_2)_2$, pale yellow tablets, m. p. 153°, and forms a dihydrazide (Curtius, Darapsky, and Müller, A., 1908, i, 145), which is convertible into a *diacetyl* derivative, m. p. 213—214° (decomp.), and readily condenses with acetone, producing a *substance*, $NO \cdot N(CH_2 \cdot CO \cdot NH \cdot N\dot:CMe_2)_2$, needles, m. p. 232° (decomp.). When treated in aqueous solution with sodium nitrite and the calculated quantity of hydrochloric acid, the nitrosohydrazide undergoes conversion into nitrosoiminodiacetic azide,
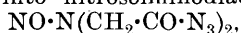
$$NO \cdot N(CH_2 \cdot CO \cdot N_3)_2,$$

a yellow oil which reacts with hydrazine hydrate, re-forming the hydrazide, and on treatment with aniline gives *nitrosoiminodiacetanilide*, $NO \cdot N(CH_2 \cdot CO \cdot NHPh)_2$, colourless needles, m. p. 224—225°. Boiling alcohol decomposes the azide in the normal manner, with formation of a *urethane* compound,

$$NO \cdot N(CH_2 \cdot NH \cdot CO_2Et)_2,$$
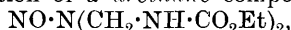
colourless crystals, m. p. 70°, which reacts readily with cold hydrochloric acid, giving an effervescence of carbon dioxide and producing anhydroformaldehyde urethane, $C_8H_{14}O_4N_2$ (Conrad and Hock, A., 1903, i, 607), but can be completely hydrolysed to ammonia, formaldehyde, carbon dioxide, and alcohol by dilute hydrochloric acid in a sealed tube or by barium hydroxide. solution; hot water causes a slow decomposition of the azide into nitrogen, carbon dioxide, a very soluble, vitreous *carbamide*,

$$NO \cdot N \overset{CH_2 \cdot NH}{\underset{CH_2 \cdot NH}{<}} \!\!\!\!> CO,$$ and a trace of azoimide. If iminodiacetic
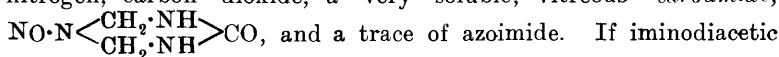
hydrazide trihydrochloride is treated in the presence of a little water with sodium nitrite, liberation of nitrogen occurs, together with the formation of *iminodiacetic azide nitrite*,

$$(N_3 \cdot CO \cdot CH_2)_2NH, HNO_2,$$
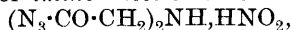
colourless needles, accompanied by the yellow nitroso-azide already mentioned; like the latter, the nitrite readily reacts with aniline, giving the nitrosoanilide.

Ethyl nitrilotriacetate (ethyl triglycollamate), prepared from the reaction product of chloroacetic acid and the additive compound of zinc chloride and ammonia or from nitrilotriacetonitrile, reacts only slowly with hydrazine hydrate, the resulting hygroscopic, vitreous *trihydrazide*, $N(CH_2 \cdot CO \cdot NH \cdot NH_2)_3$ (*tetrahydrochloride*), being converted by acetone and benzaldehyde into *condensation* products, $N(CH_2 \cdot CO \cdot NH \cdot N{:}CMe_2)_3$, small, colourless rods, m. p. 205° (decomp.), and $N(CH_2 \cdot CO \cdot NH \cdot N{:}CHPh)_3$, an amorphous powder, m. p. 206° (decomp.), respectively; the former can be converted into the latter by treatment with benzaldehyde. The addition of sodium nitrite to an aqueous solution of the nitrilotriacetic hydrazide hydrochloride causes immediate effervescence and formation of explosive leaflets of *nitrilotriacetic azide*,

$$N(CH_2 \cdot CO \cdot N_3)_3,$$
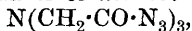
together with a sparingly soluble substance, probably a hydraziazide.   D. F. T.

Preparation of Trialkylethanolarsonium Hydroxides and their Salts. Chemische Werke Grenzach (D.R.-P., 303032, 1916; from *Chem. Zentr.*, 1918, i, 498).—By hydrolysis of halogenethyltrialkylarsonium haloids with water at higher temperatures, it is possible to produce arsonium compounds analogous to choline, and having valuable therapeutic properties. Trimethylarsine and ethylene bromide react at 100—105°, yielding *trimethyl-β-bromoethylarsonium bromide*, prismatic tablets, m. p. 239° (corresponding *picrate*, m. p. 189°), which is converted by water at 180° into *trimethylethanolarsonium bromide*, C_5H_4OBrAs, deliquescent prisms, m. p. 219°. *Triethyl-β-bromoethylarsonium bromide*, m. p. 225°, obtained from triethylarsine and ethylene bromide, on treatment with water at 180°, yields *triethylethanolarsonium bromide*, needles.   D. F. T.

Preparation of Benzenesulphonic Acid. J. W. Aylsworth (U.S. Pat. 1260852).—Excess of benzene is heated with sulphuric acid in a closed vessel, at a temperature increasing progressively during several hours from 70° to 120°. The mass is then cooled below 70°, and, while stirring, a quantity of sulphur trioxide sufficient to combine with the water present is added, and the whole is again heated as before, the series of operations being repeated as many times as is necessary.   A. S'.

Preparation of *p*-Cymenesulphonic Acid. Rheinische Campher-Fabrik (D.R.-P., 303095, 1916; from *Chem. Zentr.*, 1918, i, 498).—2-Bromo-*p*-cymene-3-sulphonic acid can be conveniently reduced by heating with ordinary or activated zinc and sodium hydroxide solution.   D. F. T.

Spinacene and some of its Derivatives. A. Chaston Chapman (T., 1918, **113**, 458—466. Compare *ibid.*, 1917, **111**, 56).—The author now assigns to spinacene the formula $C_{29}H_{48}$. It has b. p. 260° (corr.)/9 mm., $D^{15}_{15} 0.8610$, $n^{20} 1.4956$, iodine value

(Wij's method) 367·9. The hexahydrochloride has m. p. 126°, and when heated at 190°, under reduced pressure, loses its hydrogen chloride, and gives a *hydrocarbon* differing from spinacene in being less unsaturated. Dry hydrogen bromide, when passed into a cooled solution of spinacene in dry ether, gives a *hexahydrobromide*, $C_{29}H_{48},6HBr$, m. p. 132°. When warmed with dilute nitric acid (1:1), spinacene gives at least two products. When distilled over sodium at a pressure of 45 mm., spinacene is decomposed somewhat, four fractions being obtained: (1) b. p. 84—88°/ 45 mm.; (2) b. p. 155—175°/45 mm.; (3) b. p. 220—275°/45 mm.; (4) b. p. 295—298°/45 mm., and a colourless, viscous residue. Fraction (1), when purified by steam distillation, had b. p. 60°/ 20 mm., and was apparently a *cyclo*dihydroterpene, which may prove to be identical with *cyclo*dihydromyrcene or with *cyclo*linaloolene.   W. G.

A New Dehydrogenation Method. Synthesis of Decacyclene, Fluorocyclene, and Chlorene, a Green Hydrocarbon. K. DZIEWONSKI and S. SUKNAROWSKI (*Ber.*, 1918, **51**, 457—465).— It has already been shown that acenaphthylene yields decacyclene when heated at 280—290° (A., 1914, i, 826). In the hope of obtaining larger quantities of the latter hydrocarbon, other condensations in this field have been investigated, and it is now shown that both compounds can be prepared most conveniently by heating acenaphthene with lead oxide in a sealed tube. A third hydrocarbon is also formed in small quantities by this method. Being deep green in colour, it is designated chlorene .

For the preparation of decacyclene, $C_{36}H_{18}$, acenaphthene (10 grams) is heated with lead oxide (3·5) for three to four hours at 370—380° in a Carius tube. Unchanged acenaphthene is removed by boiling the product with alcohol, greenish-brown impurities by means of cold benzene, most of the fluorocyclene by boiling benzene, and most of the decacyclene by boiling cumene. The yield of the latter is 30—35%. For the preparation of fluorocyclene in a yield of as much as 25%, acenaphthene is heated with three times its weight of lead oxide for twenty hours at 330—340°, the tube being cooled to 110° every few hours and opened to let the steam escape. Fluorocyclene, $C_{48}H_{28}$, crystallises in small, orange-yellow rhombohedra belonging to the triclinic system, m. p. 396—397°.

The third hydrocarbon is found among the greenish-brown " impurities " and is formed in largest amount by heating acenaphthene with three times its weight of lead oxide for five to eight hours at 350°. It is isolated by protracted treatment with benzene and light petroleum in the cold, being more soluble in the mixture than certain yellow by-products. *Chlorene*, $C_{48}H_{26}$, crystallises in small, dark green scales, which shrink at about 265°, but are not molten at 300°. Dilute solutions are pure deep green in colour, but become brownish-red on exposure to sunlight. Concentrated solutions appear purple-red by a bright transmitted light. The spectrum shows the following absorption bands: $\lambda = 648$—600 $\mu\mu$, **very dark**

and well defined; 550—546, much paler; 490 to the end of the visible violet, a faint band. J. C. W.

The Replacement in Amides of an Alkylanilino-group by an Aniline group by Heating with Aniline Hydrochloride. G. DE BRUIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 983—985).—When 2 molecules of aniline are heated at 190° with 1 molecule of phenylmethylcarbamyl chloride, *s*-diphenylcarbamide is obtained. This substance is also formed when methyl carbanilide is heated with aniline hydrochloride. Replacement of the alkylaniline group is also found to occur when dimethyl- and diethyl-carbanilides are heated with aniline hydrochloride, and in similar circumstances, dimethyloxanilide gives oxanilide.

The replacement does not take place at lower temperatures, for when an ethereal solution of 1 molecule of phenylmethylcarbamyl chloride is heated with 2 molecules of aniline, the product obtained is methylcarbanilide. H. M. D.

Production of Aryl Sulphites. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P., 303033, 1916; from *Chem. Zentr.*, 1918, i, 499). —Aromatic sulphites are obtainable by treating aromatic hydroxyl compounds with thionyl chloride in the presence of pyridine or other suitable organic bases; the hydroxy-acids do not show this behaviour. Phenyl sulphite, b. p. 185°/15 mm. (in hydrogen); o-*tolyl sulphite*, $SO(O \cdot C_6H_4Me)_2$, b. p. 192° (corr.)/13 mm.; m-*tolyl sulphite*, b. p. 195—196° (corr.)/12 mm.; and p-*tolyl sulphite*, b. p. 199° (corr.)/12 mm., were obtained by the interaction of phenol or the cresol with thionyl chloride in the presence of pyridine and carbon disulphide; they are very stable towards water and aqueous alkalis, whereas some of their homologues, especially such as contain negative groups, readily undergo decomposition. The following compounds of this type were also prepared: *thymyl sulphite*, $SO(O \cdot C_6H_3Pr^\beta Me)_2$; *a-naphthyl sulphite*, $SO(O \cdot C_{10}H_7)_2$, indistinct crystals, m. p. 92—93°; *β-naphthyl sulphite*, nacreous powder, sensitive to water; p-*chlorophenyl sulphite*, $SO(O \cdot C_6H_4Cl)_2$, b. p. 213—214°/12 mm., solidifiable to a crystalline solid. D. F. T.

[p-**Acetylaminophenyl Allyl Ether.**] SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1263238).—p-*Acetylaminophenyl allyl ether*, leaflets, m. p. 94°, readily soluble in alcohol, ether, or acetone, but less readily so in hot water, acts as a narcotic, having also sedative and antineuralgic properties. T. F. B.

[**Preparation of Bromodiethylacetylurethanes of *N*-Acylated p-Aminophenols.**] FARBENFABRIKEN VORM. FRIEDRICH BAYER & Co. (Brit. Pat. 114680; U.S. Pat. 1256293 [SYNTHETIC PATENTS Co.]).—Compounds of the general formula

$$CEt_2Br \cdot CO \cdot NH \cdot CO \cdot O \cdot Aryl \cdot NH \cdot Acyl,$$
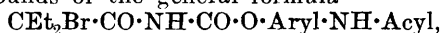
are obtained by the interaction of *N*-acyl derivatives of p-aminophenols and bromodiethylacetylcarbimide, or of p-acylaminophenol-

urethanes and bromodiethylacetyl haloids. The bromodiethylacetyl-urethane of *p*-acetylaminophenol, white leaflets, m. p. 144°, is almost tasteless, and is readily soluble in alcohol or acetone, sparingly so in benzene, ether, or water. The bromodiethylacetyl-urethane of *p*-hydroxyphenylcarbamide melts at 187°. The compounds are of value as nervines and sedatives.   A. S.

Compounds of Bivalent Cobalt with Catechol. R. F. WEINLAND and ANNA DÖTTINGER (*Zeitsch. anorg. Chem.*, 1918, 102, 223—240).—Compounds have already been described in which the catechol residue ($C_6H_4O_2$) is combined with ferric iron (A., 1912, i, 184, 445) or aluminium (A., 1914, i, 525) to form a complex anion. A series of similar catechol derivatives containing cobalt is now described, a number of ammonium, pyridine, and potassium salts of the complex acid having been prepared. The salts are obtained, in general, by addition of alkali or base to an aqueous solution containing catechol and a suitable cobalt salt, for example, sulphate or acetate, in the requisite proportions. The composition of the precipitated salt depends principally on the quantity of base or alkali added; one or two molecular proportions of alkali throw down the complex cobalto-acid, whilst increasing quantities transform this into a complex salt.

The following five compounds were obtained when ammonia was used as a precipitant. In the formulæ, R stands for the catechol residue ($C_6H_4O_2$):

I. $[CoR_2]H_2,5\frac{1}{2}H_2O$, bright red, four- or six-sided prisms, sparingly soluble in water. It is produced by the further action of ammonia on V.

II. $[CoR_2](NH_4)_2$, red, slender, rectangular prisms, very sparingly soluble in water. It is formed by the action of excess of ammonia on V.

III. $3[CoR_2]H·NH_4 + [CoR_2](NH_4)_2,H_2O$, bright red crystal aggregates, sparingly soluble in water. The salt is stable in contact with its mother liquor, but quickly decomposes after separation therefrom.

IV. $[CoR_3](NH_4)_4,C_6H_4(OH)_2$, pale red, thin tablets, easily soluble in water. The isolation of this and the previous compound requires special precautions, for which the original must be consulted.

V. $Co_3R_2(OH)_2,6H_2O$, a pale red, sparingly soluble powder, always precipitated first when ammonia is added to a solution containing catechol and a cobalt salt.

Only a single compound was obtained when pyridine was substituted for ammonia.

VI. $4[CoR_2]H_2,(C_5H_5N)_2,C_6H_4(OH)_2$, a sparingly soluble, flesh-coloured, minutely crystalline precipitate.

Compounds I. and V. can both be obtained by addition of potassium hydroxide solution in limited quantity to a catechol-cobalt solution. Using increased quantities of the hydroxide, two potassium salts were obtained.

VII. [CoR₂|KH,2H₂O, red to bluish-violet, thin oblong tablets, easily soluble in water to a dirty green solution.

VIII. [CoR₃]K₄,4H₂O, red , slender, four-sided, rectangular prisms, very soluble in water. The salt is formed only in very strongly alkaline solutions (1Co : 3C₆H₄(OH)₂ : 40KOH).

By merely warming a solution of cobalt acetate with catechol, a red, crystalline precipitate is formed, but this has not been investigated.

All the above compounds darken quickly on exposure to air, except the pyridine salt. They are stable to alkalis, in which they dissolve with a reddish-violet colour. Ammonium sulphide decomposes them with precipitation of cobalt sulphide, and they are also decomposed on boiling with potassium cyanide, potassium cobalticyanide being formed. The complex cobalt-catechol anion is, therefore, less stable than the ferri-catechol anion, which is not decomposed by these reagents. The cobalto-salts do not show the intense colour characteristic of the ferric salts.

The constitution of the salts is discussed and co-ordination formulæ are suggested.   E. H. R.

Action of Aromatic Alcohols on Aromatic Compounds in the Presence of Aluminium Chloride. II. Ralph C. Huston and Theodore E. Friedemann (*J. Amer. Chem. Soc.*, 1918, **40**, 785—793. Compare A., 1917, i, 19).—When aluminium chloride is added to a mixture of phenylmethylcarbinol and benzene at such a rate that the temperature is maintained at 25—35°, the reagents being in molecular proportions, *as*-diphenylethane is obtained in approximately 20% yield, together with ethylbenzene, diphenylmethane, and anthracene, these by-products being formed by the further action of aluminium chloride. By keeping the temperature below 10° and using only a semi-molecular proportion of aluminium chloride and a five-fold molecular proportion of benzene, the yield of diphenylethane is raised to 65%.

Phenylethylcarbinol, benzene, and aluminium chloride in molecular proportions at 35—40° yield 23—25% of *aa*-diphenylpropane, together with propylbenzene, diphenylmethane, and anthracene; by modifying the conditions, as in the preceding case, the yield of diphenylpropane can be raised to 40% of the theoretical.

Benzhydrol reacts with benzene (5 mols.) and aluminium chloride (1 mol.) at 35—40°, giving a yield of 40% of triphenylmethane, accompanied by diphenylmethane; with the reaction effected below 10°, the yield of triphenylmethane is 65—70%.

                                        D. F. T.

Preparation of a Derivative of Hexamethylenetetramine. Leo Egger (D.R.-P., 303450, 1915; from *Chem. Zentr.*, 1918, i, 499).—Hexamethylenetetramine o-acetoxybenzoate,

$$OAc\cdot C_6H_4\cdot CO_2\cdot C_6H_{12}N_4,$$
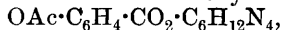
m. p. 118—119°, is prepared by the gradual addition of hexamethylenetetramine (1 mol.) to a solution of o-acetoxybenzoic acid (1 mol.) in a restricted volume of ether.   D. F. T.

Preparation of Tropic Acid. CHEMISCHE WERKE GRENZACH (D.R.-P., 302737, 1917; from *Chem. Zentr.*, 1918, i, 396).—Ethyl hydroxymethylenephenylacetate is reduced to ethyl tropate and hydrolysed, the resulting tropic acid being identical with the product obtained from atropine.   D. F. T.

A New Method for the Preparation of Aldehydes. I. KARL W. ROSENMUND (*Ber.*, 1918, **51**, 585—594).—The author has discovered the conditions whereby acyl chlorides can be converted into the corresponding aldehydes by means of hydrogen in the presence of a catalyst. The method gives excellent results and promises to be the best yet devised for the preparation of aldehydes.

The best conditions are far from what might have been predicted. The most suitable catalysts are palladinised barium sulphate containing about 5% of metal, and Kelber's nickel catalyst (A., 1917, ii, 215). The chloride is dissolved in three to five times its volume of dry xylene or cumene, which are usually regarded as "poisonous" to catalysts, and the solution is actually boiled in a reflux apparatus, hydrogen being bubbled through the while and the hydrogen chloride escaping. Even if the chloride contains traces of phosphoryl chloride, the reduction proceeds smoothly. The aldehyde is subsequently removed by means of sodium hydrogen sulphite or distillation, and the yields are often very high.

As examples, the following preparations are described; benzaldehyde from benzoyl chloride, yield 97%; butyraldehyde from butyryl chloride, yield 50%; stearaldehyde from stearyl chloride; p-*methylcarbonatobenzaldehyde*, $CO_2Me·O·C_6H_4·CHO$, radial aggregates of needles, m. p. 18·5° (*phenylhydrazone*, m. p. 157—158°), from p-methylcarbonatobenzoyl chloride, yield 95%.   J. C. W.

A New Method for the Preparation of Aldehydes. II. Synthesis of Gallaldehyde. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, **51**, 594—602).—The carbomethoxy- and acetyl derivatives of gallic acid are converted into the chlorides, these reduced to the aldehydes by the new method (preceding abstract), and then hydrolysed to gallaldehyde.

3 : 4 : 5-*Trimethylcarbonatobenzaldehyde*, $CHO·C_6H_2(O·CO_2Me)_3$, is a resinous mass, and its p-*nitrophenylhydrazone* is also viscous. 3 : 4 : 5-*Triacetoxybenzaldehyde*, from triacetylgalloyl chloride (this vol., i, 173), is also resinous, but its p-*nitrophenylhydrazone* separates in lemon-yellow, cruciform groups of fan-like crystals, m. p. 186—187° (decomp.). These aldehydes are hydrolysed in an atmosphere of hydrogen, the former by means of $2N$-sulphuric acid at 0°, the latter by boiling with alcoholic potassium acetate. *Gallaldehyde* (3 : 4 : 5-*trihydroxybenzaldehyde*) crystallises from water with $1H_2O$, which it slowly loses in a desiccator, becoming yellow. It has m. p. 212° (decomp.), does not precipitate gelatin. reduces ammoniacal silver and Fehling's solutions immediately, develops a golden-yellow colour when shaken with calcium cyanide solution, and an inky-blue with ferric chloride. The p-*nitro-*

phenylhydrazone forms golden-yellow, feathery needles, m. p. 234—236° (decomp.), but the aldehyde is so strongly acidic that it also yields a p-*nitrophenylhydrazine* salt of its p-*nitrophenylhydrazone*, in bundles of stout, yellowish-red needles, m. p. 202—204° (decomp.). On methylation with methyl sulphate, the aldehyde yields the known 3 : 4 : 5-trimethoxybenzaldehyde (Mauthner, A., 1908, i, 348).

Nierenstein (A., 1909, i, 402) believed he had isolated gall-aldehyde by the hydrolysis of acetylleucotannin, but according to his account it separated spontaneously from a solution containing not more than 1% of the aldehyde in alkali carbonate. As the aldehyde is more acidic than acetic acid, and freely soluble in water and alkali carbonates, it is improbable that Nierenstein encountered the compound.   J. C. W.

Preparation of Salts of Anthraquinonesulphonic Acids.

THE BARRETT CO. (U.S. Pat. 1260535).—Anthraquinonemonosulphonic acid may be separated from the disulphonic acids by treating a solution of the acids with sodium sulphate, whereon the monosulphonic acid is precipitated as its sparingly soluble sodium salt.   A. S.

Constituents of Essential Oils. Betulol.

F. W. SEMMLER, K. G. JONAS, and W. RICHTER (*Ber.*, 1918, **51**, 417—424).—From an examination of betulol, an ingredient of birch bud oil (compare von Soden and Elze, A., 1905, i, 451), the conclusion is drawn that the compound is a bicyclic sesquiterpene alcohol of the terpene type.

Betulol, $C_{15}H_{24}O$, has b. p. 157—158°/13 mm., D^{16} 0·9777, n_D^{16} 1·5150, a_D^{16} −26·5°, and betulyl acetate (*ibid.*) has b. p. 158—165°/10 mm., D^{20} 0·9854, n_D^{20} 1·4962, $[a]_D^{20}$ −12°. Betulol slowly absorbs hydrogen in the presence of platinum, yielding *tetrahydrobetulol*, b. p. 153—158°/14 mm., D^{18} 0·9415, n_D^{18} 1·4908, a_D^{18} −6·8°, and a small quantity of bicyclic *tetrahydrobetulene*, $C_{15}H_{28}$, b. p. 118—120°/11 mm., D^{18} 0·8737, n_D^{18} 1·4744, a_D^{18} −3°, this being derived from the product of the elimination of water from betulol. *Betulyl chloride*, obtained by means of phosphorus pentachloride, has b. p. 160—170°/11 mm., D^{21} 1·0145, n_D^{21} 1·5208, a_D^{21} +9·4°, but this is obviously a mixture, for it yields an inseparable mixture of bi- and tri-cyclic *betulenes*, $C_{15}H_{24}$, on pouring its alcoholic solution on hot sodium. The molecular refraction of the latter mixture affords the clue to this, and it is explained by the fact that hydrogen chloride, generated during the action of the phosphorus pentachloride, effects ring closure to a certain extent. Treatment of the chloride with calcium oxide at 95° also indicates the presence of a mixture, for the products are bicyclic *dehydrobetulene*, $C_{15}H_{22}$, b. p. 112—114°/9 mm., D^{23} 0·9186, n_D^{23} 1·5052, a_D^{23} −68°, and tricyclic *betulol*, $C_{15}H_{24}O$, which crystallises in silky needles, m. p. 147—148°, b. p. 160—166°/13 mm., and forms an *acetate*, b. p. 170—176°/13 mm., D^{22} 1·0290, n_D^{22} 1·5046, a_D^{22} +10°.   J. C. W.

Japanese Oil of Peppermint. HEINRICH WALBAUM (*J. pr. Chem.*, 1917, [ii], **96**, 245—250).—By the hydrolysis of the fraction of Japanese peppermint oil, b. p. 250—310°, D^{15} 0·9490, there is obtainable Δ^γ-hexen-α-ol, CHEt:CH·CH$_2$·CH$_2$·OH, b. p. 55—56°/9 mm., 156—157°/atmos. press., D^{15} 0·8508, n_D^{20} 1·48030, the constitution of which is proved by its oxidation with potassium permanganate to propionic acid; Δ^β-*hexenaldehyde*, b. p. 140—155° (*semicarbazone*, m. p. 163°), and the oily Δ^β-hexenoic acid, b. p. 215—218° (Fittig and Baker, A., 1895, i, 206, give b. p. 216—217°), are also obtained, together with the hexenyl hexenoate, on oxidation of the alcohol with chromic acid. The hexenyl alcohol is present in the peppermint oil in the form of Δ^β-*hexenyl phenylacetate*, $C_{14}H_{18}O_2$; the pure, synthetically prepared ester is a liquid of clinging, onion-like odour, b. p. 135—136°/4 mm., 299°/760 mm., D^{15} 1·000, n_D^{20} 1·49810; the *benzoate*, b. p. 134—135°/6 mm., D^{15} 1·0083, n_D^{20} 1·50560, possesses a fainter odour than the phenylacetate; the *acetate*, b. p. 75—76°/23 mm., D^{15} 0·9077, n_D^{20} 1·42355, has a pleasant odour·recalling radishes, whilst the *formate*, b. p. 66°/35 mm., D^{15} 0·9149, n_D^{20} 1·42685, has a similar but rather more pungent odour; the *hydrogen phthalate*, $C_{14}H_{16}O_4$, is an oil, the *silver* salt of which crystallises in prisms. With phenylcarbimide, the hexenyl alcohol yields no solid product, but when treated with naphthylcarbimide, a crystalline *naphthylurethane*, $C_{17}H_{19}O_2N$, m. p. 70—71°, is obtained. D. F. T.

Saponins. L. SPIEGEL and ARTHUR MEYER (*Ber. Deut. pharm. Ges.*, 1918, **28**, 100—126).—An examination of the saponin mowrin, obtainable from the seeds of *Bassia longifolia* (Mowrah seeds), the results of which diverge considerably from those of Moore, Sowton, Baker-Young, and Webster (A., 1910, ii, 228).

Crude mowrin consists mainly of a substance approximating to the composition $C_{42}H_{68}O_{25}$, easily soluble in alcohol, together with a sparingly soluble substance approximating to $C_{42}H_{68}O_{27}$. On hydrolysis with aqueous mineral acid, the main constituent gives rise to lævulose, arabinose, and mowric acid, the latter comprising a crystalline *mowragenic acid*, $C_{19}H_{28}O_5$ (*sodium* salt sparingly soluble), and an amorphous, *mowrageninic acid*, $C_{19}H_{30}O_6$. By effecting the hydrolysis of mowrin with dilute acetic acid, it is possible to detect an intermediate product, namely, a pentoside, probably of the composition $C_{29}H_{50}O_{16}$. The ease with which mowrin undergoes hydrolysis is shown by the fact that on benzoylation it and mowric acid yield the same benzoyl derivative, whilst the product obtained on acetylating mowrin with sodium acetate and acetic acid appears to be derived from the above intermediate pentoside compound.

On treatment with manganese dioxide and sulphuric acid, mowric acid undergoes oxidation and polymerisation with formation of *didehydromowric acid*, $C_{38}H_{46}O_9$, m. p. 163°, whereas hot 35% nitric acid produces *nitrodehydromowric acid*, $C_{19}H_{23}O_5·NO_2$, m. p. 207°, the reduction of which with stannous chloride gives a *hydroxydehydromowric acid*, $C_{19}H_{23}O_5·OH$, m. p. 200° (*trimethyl* deriv-

ative, m. p. 183°; *diethyl* derivative, m. p. 136°). More energetic nitration of mowric acid gives rise to a nitro-compound,

$$C_{17}H_{21}O_5 \cdot NO_2$$

or $C_{17}H_{19}O_5 \cdot NO_2$, m. p. 210°. which is reducible to a hydroxy-*compound*, $C_{17}H_{19}O_5 \cdot OH$, m. p. 170° (*trimethyl* derivative, m. p. 142°; *diethyl* derivative, m. p. 150°). This nitro-compound is oxidisable by hydrogen peroxide and by potassium permanganate with sulphuric acid, giving substances $C_{17}H_{18}O_5(OH)_2$, m. p. 125°, and $(C_{17}H_{19}O_6)_2O$, m. p. 164°, respectively, whilst hydriodic acid converts its reduction product into a substance $C_{17}H_{21}O_5I$ or $C_{17}H_{23}O_5I$, m. p. 174°. Fusion with potassium hydroxide converts mowric acid into a *substance* $C_{14}H_{18}O_3$, m. p. 181° (*methyl* derivative, m. p. 160—175°). D. F. T.

The Action of Sunlight on Coumarin. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 875—876. Compare Ciamician and Silber, A., 1914, ii, 234).—A preliminary account of experiments which indicates that the product of sunlight on coumarin is not the hydrodicoumarin which was obtained synthetically by Fittig and Dyson in 1889 (compare Dyson, T., 1887, **51**, 66). S. B. S.

Synthesis of Pyranol Derivatives. SARAT CHANDRA CHATTERJI and BROJENDRA NATH GHOSH (T., 1918, **113**, 444—449). —Diketohydrindene condenses with *o*-hydroxyaldehydes, giving ketoindopyranol derivatives (compare T., 1915, **107**, 1442), this reaction being due, apparently, to the presence of the group ·CO·CH₂·CO· in the diketohydrindene. In order to show that the reaction is a general one, two other ketones, benzoylacetone and acetylacetone, containing this group have been condensed with salicylaldehyde.

Benzoylacetone, when condensed with salicylaldehyde in methyl alcohol solution in the presence of hydrogen chloride, gave 3-*acetyl-2-phenyl*-1 : 4-*benzopyranol anhydrohydrochloride* and 3-*benzoyl-2-methyl*-1 : 4-*benzopyranol anhydrohydrochloride*, together with a third *compound*, $C_{27}H_{20}O_3, \frac{1}{2}H_2O$, m. p. 120°.

With acetylacetone, salicylaldehyde gave a *compound*, $C_{17}H_{16}O_3$, violet prisms soluble in acetic acid, giving a *hydrochloride*, a *phenylhydrazone*, m. p. above 300°, and an insoluble *compound*, $C_{24}H_{22}O_5$. [For experimental details, see the original.] W. G.

The Cinchona Alkaloids. XIX. Partial Synthesis of Quinine. PAUL RABE and KARL KINDLER (*Ber.*, 1918, **51**, 466—467. Compare A., 1911, i, 742).—Quinicine (quinotoxine) reacts with sodium hypobromite to form N-*bromoquinicine*, m. p. 123°. This is converted into quininone by treatment with alkali hydroxide, and the ketone is reduced to quinine by means of aluminium powder and sodium ethoxide solution. Considering only the groups affected, the synthesis is represented thus:

$$\begin{array}{ccc} =NH & =NBr & =N-CH- & =N-CH- \\ CH_2- & CH_2- & CH- & CH- \\ CO- & CO- & CO- & HO \cdot CH- \end{array}$$

J. C. W.
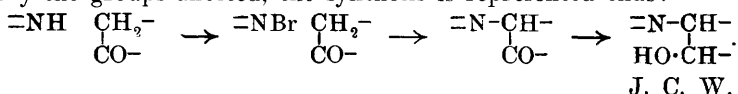
α-**Hydroxycinchonine.** E. Léger (*Compt. rend.*, 1918, **166,** 903—906).—As a result of a study of the behaviour of α-hydroxycinchonine (compare Jungfleisch and Léger, A., 1888, 380, 508; 1889, 906), the author considers that the hydroxyl group is in the side chain, the double linking in the vinyl group being satisfied during the process of hydration. α-Hydroxycinchonine thus has the constitution $CH_3 \cdot CH(OH) \cdot [C_{16}H_{17}(CH \cdot OH)N_2]$. The grouping $CH_3 \cdot CH(OH) \cdot$ is preferred to $CH_2(OH) \cdot CH_2 \cdot$, since the compound yields (1) iodoform by the action of sodium hydroxide and iodine, and (2) carbon tetrabromide by the action of hypobromous acid.

W. G.

Cevadine [Veratrine]. III. MARTIN FREUND and ADOLF SCHWARZ (*J. pr. Chem.*, 1917, [ii], **96**, 236—244. Compare A., 1904, i, 613).—As the author has been unable to confirm the results described earlier (*Zeitsch. Ver. deutsch. Chem.*, 1909, **22**, 2472) on the degradation of cevine, these are withdrawn. When cevine methiodide, $C_{27}H_{43}O_8N,MeI,2H_2O$, decomp. 257° (Freund and Schwarz, A., 1899, i, 465), is treated with silver oxide and water, it undergoes conversion into des-N-*methylcevine*, $C_{28}H_{45}O_8N,H_2O$, crystalline scales, decomp. at 277° (accompanied by an uncrystallisable yellow oil), which absorbs atmospheric carbon dioxide, with formation of a hydrogen carbonate, and yields crystalline salts resistant to aqueous ammonia or sodium carbonate; the *hydriodide* (1H₂O), decomp. at 256°, *hydrobromide*, with 1H₂O, decomp. at 271—273°, *hydrochloride*, decomp. at 258—261°, and *picrate*, with 3H₂O, were prepared. Methyl iodide at 60—70°, cyanogen bromide, phenylhydrazine, hydroxylamine, semicarbazide, thiosemicarbazide, and aqueous hydrogen peroxide left the cevine molecule intact. Treatment of a methyl-alcoholic solution of de-*N*-methylcevine hydrochloride with silver oxide yields an alkaline solution, which, on evaporation, leaves an oily residue; this, on the addition of alkali and warming, changes into the crystalline solid base, the behaviour being suggestive of a tautomeric change from a true ammonium base to a pseudobase.

Examination of cevadine, cevine, and dibenzoylcevine by Zerewitinoff's method with a solution of methyl magnesium iodide in *iso*amyl ether indicates the presence of four, six, and six hydroxyl groups respectively, the unexpected value for the last figure being at present without explanation.

D. F. T.

Ricinine. BRUNO BÖTTCHER (*Ber.*, 1918, **51**, 673—687).—The most important study of ricinine, the alkaloid of castor-oil seeds, which has appeared so far is that by Maquenne and Philippe, who went so far as to assign the formula (I) to the compound (A., 1905, i, 80). In view of the very unusual three-membered nitrogen-carbon ring in this formula, the author has

made a fuller examination of ricinine, and proposes the formula (II):

$$NMe<^{C(CO_2Me):C}_{CH=CH\cdot C}>N$$

(I.)

$$\begin{array}{c} CO_2Me\cdot C===C\cdot CH \\ | \quad\quad N \quad || \\ | \quad\quad || \quad || \\ NMe\cdot C\cdot CH \end{array}$$

(II.)
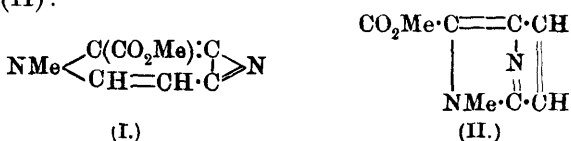
This accords with the behaviour of ricinine at one and the same time as the ester of a pyridinecarboxylic acid and as a glyoxaline.

The alkaloid is obtained by extracting the residue of the seeds with boiling water, after removing the oil, evaporating the extract to dryness under reduced pressure, and exhausting the powder with alcohol. From 300 kilos. of seed, about 450 grams of crude alkaloid may be obtained. The pure compound has m. p. 200—201°, reduces permanganate at once, is not affected by nitric acid, and, like histidine, gives Weidel's reaction. On hydrolysis with dilute potassium carbonate, it yields ricininic acid, m. p. 296—298° (decomp.), which forms a *silver* salt, from which ricinine may be recovered by means of methyl iodide. The acid may be reduced by means of 5% sodium amalgam to *dihydroricininic acid*, which crystallises from water in white needles, m. p. 245° (if quickly heated), 255° (if slowly heated), which give an intense violet coloration with ferric chloride, characteristic of glyoxaline-carboxylic acids. The *methyl* ester (*dihydroricinine*), prepared from the *silver* salt, but not by reducing ricinine itself, crystallises in glistening needles or plates, m. p. 160°, and is much more easily hydrolysed than ricinine. The failure to obtain a tetrahydro-derivative is an argument in favour of formula (II) as against (I); the ethylene linking in the glyoxaline ring is, as usual, unaffected by sodium amalgam.

Ricininic acid is oxidised by chromic acid and dilute sulphuric acid to methylamine, oxalic acid, and hydrogen cyanide, the evolution of this being quantitative, one molecule per molecule of acid, and characteristic also of histidine. Hypobromite solutions apparently cause saturation of the ethylene linking, a *compound*, m. p. 256—257° (decomp.), represented by the formula $HBrO,C_7H_6O_2N_2$ (ricininic acid), crystallising on acidifying. Distillation with zinc dust furnishes a dipyridyl (*aurichloride*, $C_{10}H_8N_2,HAuCl_4$, decomp. 250°) and a pyrrole derivative. Distillation with lime also gives a pyrrole compound, which is another established reaction of histidine.

Ricininic acid is degraded to 3-hydroxy-1-methyl-1 : 4-dihydro-pyrid-4-one, $NMe<^{CH==CH}_{CH:C(OH)}>CO$, by means of fuming hydrochloric acid at 150° (the best method; see Maquenne and Philippe. A., 1904, i, 339), or by hydrolysis with alkali hydroxides. If heated with 50% sulphuric acid, an *acid* is produced, m. p. 216° (decomp.), which contains one NMe group, gives the reddish-brown colour with ferric chloride characteristic of pyridine-carboxylic

acids, yields a pyrrole on distillation with lime, and forms the above pyridone on heating with hydrochloric acid at 150°. The pyridone does not give the pyrrole reaction on distillation with lime. J. C. W.

Synthesis of α-Piperidylethylalkine (2-α-Hydroxypropyl-piperidine). LUDWIG LAUTENSCHLÄGER and ARVID G. T. ONSAGER (*Ber.*, 1918, **51**, 602—605).—Pyridine-2-aldehyde (Harries and Lénárt, A., 1915, i, 970) is converted into 2-α-hydroxypropyl-pyridine, b. p. 214—216° (Engler and Bauer, A., 1891, 1505) by means of magnesium ethyl bromide, and this is reduced by sodium and alcohol to 2-α-hydroxypropylpiperidine, which crystallises from light petroleum in leaflets, m. p. 99—100°, and needles, m. p. 69—70° (*ibid.*, 1894, i, 471). A small quantity of *r*-coniine is formed as well. J. C. W.

Transformation of Unimolecular N-Alkyldihydroquin-aldine Picrates. GUSTAV HELLER (*Ber.*, 1918, **51**, 437—439).— The picrates of 1:2-dimethyl- and 2-methyl-1-ethyl-1:2-dihydro-quinoline (A., 1915, i, 300; and Freund, A., 1905, i, 151; 1909, i, 417) suffer rearrangement on crystallisation from acetone and light petroleum into bright red *isomerides* (1-methyl-, m. p. 148°; 1-ethyl-, m. p. 128°). These do not yield the parent bases on treatment with sodium hydroxide, but change into the *sodium* salts of third, acidic *isomerides* (1-methyl-, m. p. 129—131°; 1-ethyl-, m. p. 136°; both pale brown granules). J. C. W.

Synthesis in the α-Naphthindole Series. J. MARTINET (*Compt. rend.*, 1918, **166**, 851—853. Compare A., 1913, i, 756).— α-Naphthylamine condenses with ethyl mesoxalate in boiling acetic acid solution to give *ethyl 3-hydroxy-2-oxynaphthindole-3-carb-oxylate* (annexed formula), m. p. 201°. The corresponding *methyl* ester has m. p. 268°. Either of these esters, when heated in a water-bath with aqueous potassium hydroxide in a current of hydrogen, and the liquid then acidified, yields *α-naphthoxindole*, m. p. 247°. These esters, when treated with aqueous potassium hydroxide in contact with air, yield potassium α-naphthisatate, from which, when the solution is acidified, α-naphthisatic acid is precipitated, which is rapidly converted into α-naphthisatin, red needles, m. p. 225° (compare Hinsberg, A., 1888, 373). Contrary to the statement of Hinsberg (*loc. cit.*), this isatin gives the indophenine reaction, and its phenyl-hydrazone has m. p. 286°, and not 270°, as stated (*loc. cit.*). W. G.
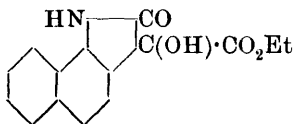
Preparation of Mercury Compounds of the Acridine Series. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (U.S. Pat. 1259517).—The mercury compounds obtained by treating acridine dyes, alkylated at the acridine nitrogen atom, with a soluble mercury salt in the presence of a solvent, are yellowish-brown powders,

giving yellowish-green solutions in water, yellowish-green fluorescence in dilute solution in alcohol, ethyl acetate, glacial acetic acid, and acetone, and an intense green fluorescence in concentrated sulphuric acid. Even in very dilute solutions they check the growth of bacteria. The mercury compound of the product obtained by heating 3 : 6-diamino-2 : 7-dimethylacridine with methyl chloride under pressure, is specially claimed. A. S.

Pyranthridone. ROLAND SCHOLL and OTTO DISCHENDORFER (*Ber.*, 1918, **51**, 441—452).—Pyranthridone (annexed formula) may be regarded as a compound intermediate between pyranthrone, $C_{30}H_{14}O_2$, and flavanthrene, $C_{28}H_{12}O_2N_2$. Its synthesis is now described. 1-Chloro-2-aminoanthraquinone (A., 1913, i, 1070) is boiled with benzaldehyde, the water produced being allowed to escape, when *1-chloro-2-benzylideneaminoanthraquinone* is formed, in pale yellow leaflets, m. p. 184°. This is boiled with 1-chloro-2-methylanthraquinone in naphthalene solution, with a little copper powder, when a mixture of dianthraquinonyls is obtained, consisting of condensation products of each of the reacting compounds separately and the desired unsymmetrical 2-benzylideneamino-2′-methyl-1 : 1′-dianthraquinonyl. After removing the solvent naphthalene by steam, the residue is dissolved in concentrated sulphuric acid, whereby the 2 : 2′-dimethyl-1 : 1′-dianthraquinonyl is unchanged, but the benzylidene residues from the other products are eliminated as benzaldehyde. The 2 : 2′-diamino-1 : 1′-dianthraquinonyl so formed immediately condenses to flavanthrene and the 2-amino-2-methyl-1 : 1′-dianthraquinonyl to 3 : 4-*phthalyl*-8 : 9-o-*benzoylene*-5-*methylphenanthridine* (annexed formula). The latter is moderately soluble in hot nitrobenzene, whereas flavanthrene is almost insoluble, and the other products are freely soluble. It crystallises in golden, rhombic leaflets, which do not melt below 450°. Reduction with hyposulphite at 30—40° gives a red vat, from which a *di*-p-*bromobenzoyl* derivative,
$$C_{29}H_{15}ON(O \cdot CO \cdot C_6H_4Br)_2,$$
small, yellow needles, m. p. 318°, may be prepared, whilst reduction with strongly alkaline solutions of hyposulphite at higher temperatures yields a blue vat, from which a *di*-p-*bromobenzoyl*-derivative, $C_{29}H_{17}ON(O \cdot CO \cdot C_6H_4Br)_2$, m. p. 210°, may be obtained.
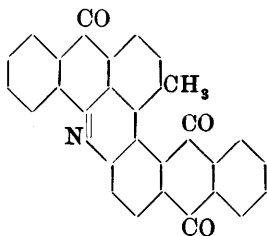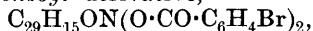
The phenanthridine derivative may be condensed to *pyranthridone* by heating alone at 360—380°, or with sulphuric acid at 160—170°, or with alcoholic potassium hydroxide. The dye crystallises from quinoline in brownish-yellow needles, which sublime on heating, but are not molten at 500°. It yields a violet-blue

vat, from which cotton is dyed orange-red after hanging in the air. A *di*-p-*bromobenzoyl* derivative, felted, orange-yellow needles, decomp. 350°, may also be obtained from the tetrahydro-compound in the vat. When heated with hydriodic acid and phosphorus, pyranthridone yields *dihydropyranthridine*, $C_{29}H_{19}N$, in pale yellow, rhombic leaflets, m. p. 302°, which is converted into the parent base, *pyranthridine*, $C_{29}H_{17}N$, reddish-brown leaflets, m. p. 370°, by passing its vapour over red-hot copper.   J. C. W.

Synthesis of Flavanthrene. R. Scholl and O. Dischendorfer (*Ber.*, 1918, **51**, 452—453).—The immediate precursor of flavanthrene in the various syntheses which have been achieved is 2 : 2′-*diamino*-1 : 1′-*dianthraquinonyl*, but this has not hitherto been isolated. It may be prepared by boiling 1-chloro-2-benzyl-ideneaminoanthraquinone with copper powder and naphthalene (compare preceding abstract), extracting the 2 : 2′-dibenzylidene-amino-1 : 1′-dianthraquinonyl so formed with cold alcohol, and leaving the solution for some time, when the benzylidene residues are spontaneously eliminated and the desired compound crystallises. It forms microscopic, red needles, and changes into flavanthrene at 250°.   J. C. W.

The Properties of the Sulphonium Compounds obtained by S. Smiles by the Condensation of Dinitrophenthiazine-sulphoxide with Aromatic Amines, Phenols, and Phenol-ethers. F. Kehrmann, S. Lievermann, and P. Frumkine (*Ber.*, 1918, **51**, 474—480).—A revision and criticism of the work of Smiles and Hilditch (T., 1908, **93**, 145). It appears that the products obtained by these workers were abnormally coloured by impurities, although their constitution was rightly interpreted. It is essential to use pure 3 : 9-dinitrophenthiazinesulphoxide, prepared as in A., 1913, i, 1231, for the condensations, and the reaction with anisole or phenetole is best brought about by shaking a mixture of the compounds with concentrated sulphuric and acetic acids (1 : 1). The phenazothionium salts so produced are converted into the free bases by precipitation with ammonia. 3 : 9-*Dinitro*-1-*anisylphenthiazine*, m. p. 248°, forms carmine-red flocks, which change in contact with the mother liquor into a green, crystalline powder with metallic lustre, and the 1-*phenetyl* compound, m. p. 230°, crystallises in groups of fiery-red prisms or dark red granules with green lustre. The free bases resemble rosindone, and their solutions exhibit a brilliant orange-yellow fluorescence, whilst solutions of their salts are pale in colour and not fluorescent. The

(I.)   (II.)
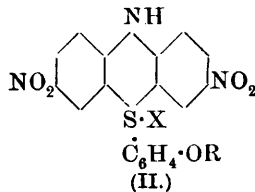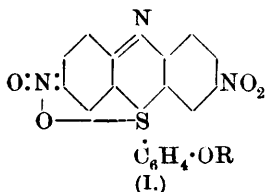
free "bases" are therefore para-quinonoid, internal phenazo-thionium salts of nitronic acid (I), whilst the salts of mineral acids (II) contain nitro-groups as the sole chromophores.

The *chloride* of the anisyl derivative forms straw-yellow granules, the *platinichloride* is pale yellow, and the *dichromate* is egg-yellow.

The anisyl compound has also been reduced by means of stannous chloride, the stannichloride so formed acetylated, and the new canary-yellow base, 3 : 9-*diacetylamino*-1-*anisylphenazothionium*, isolated as the *hydrogen carbonate*, which forms satiny scales, the *platinichloride* being very pale yellow. J. C. W.

Syntheses in the Isatin Series. "Definitive Enzymic Synthesis." GUSTAV HELLER (*Ber.*, 1918, **51**, 424—437).— *N*-Sodioisatin reacts readily with organic chlorides at moderate temperatures in the presence of benzene. Thus, acetyl chloride yields *N*-acetylisatin, m. p. 141°; benzenesulphonyl chloride gives N-*benzenesulphonylisatin*, in pale yellow, slanting prisms, m. p. 186·5—187°; carbonyl chloride forms *carbonyldi-isatin*,

$$\underset{CO\cdot CO}{\overset{C_6H_4}{>}}N\cdot CO\cdot N\underset{CO\cdot CO}{\overset{C_6H_4}{<}},$$

in long, yellow needles, m. p. 218° (decomp.); ethyl chloroformate yields *ethyl isatin*-1-*carboxylate*, in yellow prisms, m. p. 117°, which forms a *dioxime*, needles, m. p. 145°, and the corresponding *methyl* ester crystallises in golden-yellow leaflets, m. p. 170°.

The latter esters undergo a remarkable change when boiled with water, left with 50% sulphuric acid or concentrated hydrochloric acid, or treated with zinc dust and acetic acid. The product is an acid with four atoms of hydrogen more than the parent 1-carboxylic compound; it does not give the indophenine reaction, but it very readily yields isatinic acid when exposed in alkaline solutions to the air. Acetaldehyde is also produced if the ethyl ester is used, and formaldehyde from the methyl ester. The acid is therefore 2 : 3-*dihydroxy*-2 : 3-*dihydroindole*-2-*carboxylic acid* (annexed formula); it forms colourless crystals, m. p. 144°, and yields a *phenylhydrazide*, pale yellow, narrow prisms, m. p. 152° (decomp.), and a *lactone*, long, yellow needles, m. p. 108°. The corresponding esters, *ethyl*, m. p. 67°, and *methyl*, m. p. 85°, are produced when the original esters are boiled with the alcohols. Acetaldehyde and formaldehyde are also produced, but the origin of the four hydrogen atoms is obscure. As a rule, it is by no means easy to convert an indole derivative into a dihydroindole compound, but the above reaction indicates that when the carbalkyloxy-group is introduced into isatin, the subsequent fixation of as many as four atoms of hydrogen, and a thorough internal rearrangement in the molecule, become very easy. The change resembles the far-reaching effects so often produced by enzymes, and the fact that acids stimulate the change only strengthens the analogy.
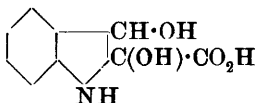
The acid undergoes another remarkable change on oxidation with potassium dichromate and dilute sulphuric acid. The product is an acid which contains an extra methylene group and yields quinaldic acid on reduction with hydriodic acid and phosphorus. It is therefore $2:4$-*dihydroxy*-$1:2:3:4$-*tetrahydroquinoline*-2-*carboxylic acid*, $C_6H_4{<}^{CH(OH)\cdot CH_2}_{NH---C(OH)\cdot CO_2H}$; it forms long needles, m. p. 127°, yields a *methyl* ester, m. p. 62°, and gives a *hydroxydihydroquinoline*-2-*carboxylic acid*, m. p. 184°, on heating with acetic anhydride and sodium acetate. This obscure case of the extension of the ring from five members to six also recalls enzyme activities.

N-Sodioisatin also reacts with ethyl oxalyl chloride, forming N-*ethyloxalato-isatin* [*ethyl isatin*-1-*glyoxylate*] (A), in pale yellow needles, m. p. 180—182°, which changes into $2:3$-*dihydroxy*-2-*ethyl-*

(A.)   (B.)
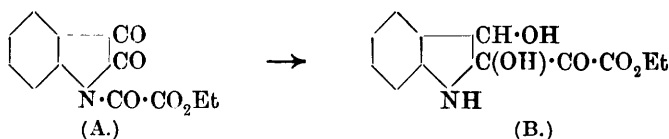
oxalatodihydroindole [*ethyl* $2:3$-*dihydroxy*-$2:3$-*dihydroindole*-2-*glyoxylate*] (B), m. p. 81°, when boiled with alcohol.   J. C. W.

Dyes Derived from Sulphazone. A Contribution to Claasz's New Theory of the Indigo Chromophore. W. HERZOG (*Ber.*, 1918, **51**, 516—521).—Sulphazone, which does not form an oxime or hydrazone, thus agreeing with the suggestion that it should be regarded as 3-hydroxybenzsulphonazine (A., 1916, i, 424), has often been used as a component in azo-dyes (A., 1912, i, 390). It has also been converted into benzsulphonazoline by the action of ammonia under pressure (Claasz, A., 1916, i, 425), and this has been used to prepare dyes which closely resemble indigotin without containing the usually accepted indigo chromophore, $-CO\cdot C\ddot{:}C\cdot CO-$. The discovery of these dyes has led Claasz to suggest that the indigo chromophore is a quinonoid, inner-salt structure of the annexed type (A., 1916, i, 840).
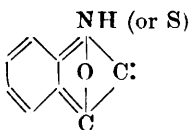
It is now shown that sulphazone itself, because of its reactive methylene group, can also form vat-dyes of the indigoid type, the tinctorial properties of which can only be ascribed to the presence of the above chromophore.

Sulphazone condenses with α-isatinanilide in boiling acetic anhydride to form the *compound* (I). This separates in deep bluish-red crystals, which sublime at above 300°, and dissolve in concentrated sulphuric acid with violet colour and in fuming acid (20% SO_3) with carmine colour. It is decomposed by alkalis after a time, but a fresh, yellowish-green solution in sodium hydroxide yields a red and finally yellow hyposulphite vat. The affinity for fibres is very small, however, and the colour on

filter paper changes from strawberry-red to dark green, probably owing to the participation of the sulphonyl group in the reduction.
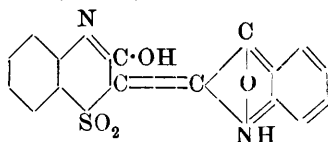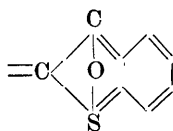
(I.)   (II.)

The *compound* (II) is obtained by condensing sulphazone with thionaphthenequinone-anilide (A., 1908, i, 200). It forms yellowish-red needles which melt and sublime at above 300°, and although it is unstable towards alkali hydroxides, it is possible to prepare a yellow hyposulphite vat.

When sulphazone is condensed with β-isatinanilide (isatin-2-anil), a compound is produced which is related to the above dye (I) as indirubin is to indigotin. The lack of tinctorial properties is ascribed to the absence of the above chromophore. The *compound* (annexed formula) forms bluish-red crystals which decompose at about 300°, and dissolve in sulphuric acid with yellowish- to reddish-brown colour. J. C. W.
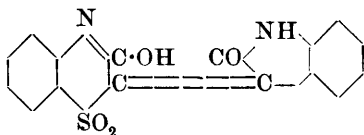
Hydantoin Derivatives. CLARENCE J. WEST (*J. Biol. Chem.*, 1918, **34**, 187—194).—The following hydantoin derivatives have been prepared by the method described by Dakin (A., 1910, i, 590). In view of Dakin's theory regarding the structure of allantoin (T., 1915, **107**, 434), it was thought that the active *dl*-hydantoins might be found to differ in physical properties from the inactivated forms. Such differences have not been observed. d-α-*Phenylcarbamidopropionic acid*, $C_{10}H_{12}O_3N_2$, crystallises in needles, m. p. 175° (decomp.), $[a]_D^{20} + 7.78°$ in acetone; d-α-*phenylmethylhydantoin*, $C_{10}H_{10}O_2N_2$, m. p. 178°, $[a]_D^{20} + 2.24°$ in $N/2$-sodium hydroxide and $-10.04°$ in acetone; dl-α-*naphthylmethylhydantoin*,

$$C_{14}H_{12}O_2N_2,$$
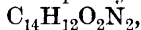
m. p. 179—180°; d-α-*naphthylcarbamidopropionic acid*, $C_{14}H_{14}O_3N_2$, needles, m. p. 198—200° (decomp.), $[a]_D^{20} + 3.80$ in $N/2$-sodium hydroxide; d-α-*naphthylmethylhydantoin*, $C_{14}H_{12}O_2N_2$, m. p. 166°, $[a]_D^{20} - 17.85°$ in acetone; α-*carbamidobutyric acid*, $C_5H_{10}O_3N_2$, m. p. 184°. The melting points of the following compounds have been determined, and found to differ from those hitherto recorded: hydantoic acid, 179—180°; *dl*-methylhydantoin, 155—156°; *dl*-α-phenylcarbamidopropionic acid, 174°; *dl*-α-phenylmethylhydantoin, 178°; α-carbamido-α-methylpropionic acid, 184°; *dl*-hydantoinacetic acid, 228—229°, and *dl*-hydantoinpropionic acid, 179—180°. H. W. B.

Constitution and Colour. VI. Triphenylmethane Dyes. F. KEHRMANN (*Ber.*, 1918, **51**, 468—474).—The constitution of

the various salts of triphenylmethane bases is discussed. Most of the facts are already known, but the theories developed are based also on the results of spectrographic observations which will be published later. The novel feature is the suggestion that the central carbon atom participates in the formation of the highest type of salts, namely, those which only exist in strongly acid solutions. The extra equivalent of acid is attached by residual or main affinities to this atom. For example, the yellow solution of triphenylmethyl chloride in a solution of hydrogen chloride in acetic acid is supposed to contain the salt, $\begin{smallmatrix}H\\Cl\end{smallmatrix}>CPh_2:\langle\overset{=}{=}\rangle\begin{smallmatrix}H\\Cl\end{smallmatrix}'$ and the golden-yellow, tetra-acid salts of magenta are written

$$(C_6H_4\cdot NH_2,HX)_2:C:\langle\overset{=}{=}\rangle:NH,HX.$$
$$\overset{\displaystyle\ }{H\quad X}$$
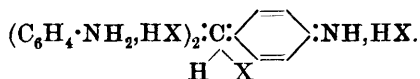
J. C. W.

Oxidative Degradation of Phloroquinyl. I. Pyrquinacridine and its Carboxylic Acids. L. T. BRATZ and ST. VON NIEMENTOWSKI (*Ber.*, 1918, **51**, 366—376).—Phloroquinyl (I) (A., 1906, i, 210) is a remarkably stable substance which can only be oxidised at all readily by means of sodium dichromate in solution in moderately concentrated nitric acid. The product of this reaction is a yellow, crystalline acid, *pyrquinacridinedicarboxylic acid* (II). It is a very sparingly soluble acid, m. p. 375°, which
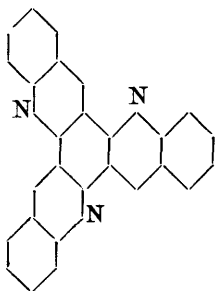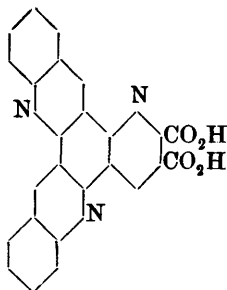
(I.)   (II.)

crystallises from much acetone in almost colourless needles with $1COMe_2$, and from boiling glacial acetic acid in very slender needles with 1AcOH, or golden-yellow prisms with 2AcOH. It dissolves readily in dilute alkali hydroxides or carbonates, ammonia, or boiling sodium acetate solution, the salts being precipitated on adding an excess of the alkaline agent; the *potassium* and *silver* salts are mentioned. Heated with acetic anhydride, the acid changes into its *anhydride*, which crystallises in silky needles, m. p. 374°, whilst treatment with 20% hydrochloric acid at 180—190° results in the formation of *pyrquinacridinecarboxylic*
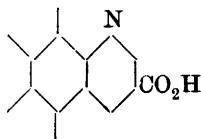
acid (annexed scheme). This is even less soluble than the dicarboxylic acid, but crystallises from nitrobenzene in very slender, curved needles, m. p. 380—382°. The *anilide*, $C_{30}H_{18}ON_4$, is obtained by cautiously heating the dicarboxylic acid with aniline, in yellow needles, m. p. 338°.

The parent substance, *pyrquinacridine*, $C_{23}H_{13}N_3$, is obtained by distilling the acids with lime. It crystallises from toluene in almost colourless, slender needles, m. p. 265°, and dissolves in concentrated acids, salts being deposited on dilution. The following are described: *hydrochloride*, $B,2HCl,2\cdot5H_2O$; *hydriodides*, $B,3HI$ (possibly, however, B,I_2,HI) and B,HI; *nitrates*, $B,3HNO_3$ and B,HNO_3. J. C. W.

The Simplest Rhoduline. F. KEHRMANN and M. RAMM (*Ber.*, 1918, **51**, 385—388).—An account of the preparation and properties of 3 : 7-diamino-5-methylphenazonium salts.

3 : 7-Diacetylaminophenazine is mixed with methyl sulphate (1 mol.) and nitrobenzene at 150°, and the product is treated with hydrochloric acid, whereby a mixture of the chlorides of three methyl derivatives is precipitated. This is repeatedly extracted with hot alcohol, which dissolves small quantities of the chloride of 2 : 8-diacetylamino-5-methylphenazonium, and the residue is hydrolysed by dissolving in sulphuric acid and cautiously mixing with water. The dark red solution is then rendered alkaline by ammonia and extracted with ether, which dissolves 3-amino-7-methylaminophenazine, when the 3 : 7-*diamino-5-methylphenazine* remaining in the red solution may be precipitated in the usual way as the *nitrate*, long, metallic-green needles, *perchlorate* (green solution in concentrated sulphuric acid, becoming violet and then red on dilution), *platinichloride*, or *dichromate*. J. C. W.

Phencyazonium Compounds. F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 388—391).—Ehrlich and Benda (A., 1913, i, 904) treated some acridine and pyronine dyes with potassium cyanide, thereby obtaining "leucocyanides," which yielded on oxidation dyes with the same properties as the corresponding azonium salts. For example, 2 : 8-diamino-10-methylacridine yields 2 : 8-diamino-5-cyano-10-methylacridine salts (I) which resemble phenylsafranine salts (II).

$$HX,NH: \qquad NH_2 \qquad\qquad HX,NH: \qquad NH_2$$
(I.)   (II.)
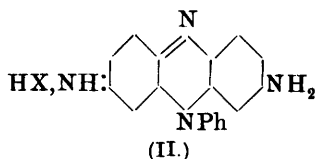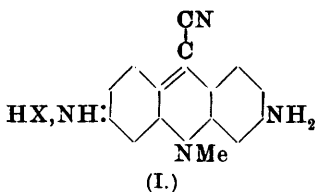
It appears, therefore, that the $:C\cdot C:N$ group has about the same

tinctorial influence as the nitrogen atom, and it seemed to be of interest to prepare the chromogen of this type.

This is obtained by oxidising Kaufmann and Albertini's 5-cyano-10-methyldihydroacridine (A., 1909, i, 606), a warm acetic acid solution being merely exposed to the air. The 5-cyano-10-methyl-acridinium salt, or "10-*methylphencyazonium*" salt, so formed may be converted into the *perchlorate*, which crystallises in yellowish-brown leaflets, and dissolves in sulphuric acid with orange-yellow colour, forming a mono-acid salt only.   J. C. W.

The Products of the Condensation of 2 : 4-Dichlorophenyl hydrazine with Aldehydes, 1 : 2-, 1 : 3-, and 1 : 4-Diketones and 1 : 3-Ketocarboxylic Esters, and their Behaviour towards Chlorine. CARL BÜLOW [with R. HUSS] (*Ber.*, 1918, **51**, 399—417).—The author has shown recently that phenylhydrazones of the type NHPh·N:C(NHR)·CO₂Et are decomposed by chlorine in cold alcohol, the phenylhydrazine residue being removed as a diazonium chloride (this vol., i, 42, 196). It appeared to be of interest, therefore, to examine the action of chlorine on simple phenylhydrazones, NHPh:CHR, and in the sequel it appears that a diazonium salt is always formed if the compound is a genuine phenylhydrazone. In fact, the non-production of a diazonium salt may be taken as strong presumptive evidence that the so-called phenylhydrazone has some other structure.

2 : 4-Dichlorophenylhydrazine was chosen as a base from which to prepare suitable hydrazones. It may be obtained by boiling ethyl α-o-toluidinoglyoxylate 2 : 4-dichlorophenylhydrazone with hydrochloric acid (*ibid.*, 197) or from 2 : 4-dichloroaniline by the usual method (Chattaway and Pearce, T., 1915, **107**, 32).

The 2 : 4-*dichlorophenylhydrazone* of o-*chlorobenzaldehyde*, C₆H₄Cl·CH:N·NH·C₆H₃Cl₂, crystallises in felted, pale yellow needles, m. p. 168—169°, and forms a yellow solution when chlorine is slowly passed into a suspension in cold alcohol. This solution contains a diazonium salt, C₆H₃Cl₂·N₂Cl, for it couples with β-naphthol or α-naphthylamine, and it yields a substance, m. p. 82—86°, on treatment with water. m-*Nitrobenzaldehyde*-2 : 4-*dichlorophenylhydrazone* forms yellow needles, m. p. 207°, and dissolves in cold alcohol when treated with chlorine, the solution almost immediately depositing a substance, m. p. 146—147°, and coupling with β-naphthol to form 2 : 4-*dichlorobenzeneazo-β-naphthol*, m. p. 188—189°. *Salicylaldehyde*-2 : 4-*dichlorophenylhydrazone* crystallises in glittering needles, m. p. 148°, and also yields a diazonium salt with chlorine. *Vanillin*-2 : 4-*dichlorophenylhydrazone*, m. p. 135°, likewise forms the diazonium salt. These hydrazones dissolve in concentrated sulphuric acid with deepening of colour, but are precipitated with the original tints if the solutions are quickly poured on ice.

Benzil yields a compound which is indifferent to chlorine. It can scarcely be, therefore, the normal "osazone," although it has the same composition, and it is probably 5 : 6-*diphenyl*-2 : 3-*di*-op-

dichlorophenyl-1 : 2 : 3 : 4-*tetrahydro*-1 : 2 : 3 : 4-*tetrazine*,

$$C_6H_3Cl_2 \cdot N \begin{matrix} \diagup N(C_6H_3Cl_2) \cdot NH \diagdown \\ \diagdown NH \underline{\hspace{1cm}} CPh \diagup \end{matrix} CPh.$$
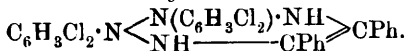
It crystallises in lemon-yellow needles, m. p. 217°.

Similarly, benzoylacetone yields 1-op-*dichlorophenyl*-5-*phenyl*-3-*methylpyrazole*, $C_6H_3Cl_2 \cdot N \begin{matrix} \diagup N = CMe \\ \diagdown CPh:CH \end{matrix}$ in snow-white needles, m. p. 95°, which is attacked by chlorine, but without producing a diazonium salt.

Ethyl diacetosuccinate gives *ethyl* 1-op-*dichloroanilino*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylate*, $C_6H_3Cl_2 \cdot NH \cdot N \begin{matrix} \diagup CMe:C \cdot CO_2Et \\ \diagdown CMe:C \cdot CO_2Et \end{matrix}$, in snow-white needles, m. p. 102°, which dissolves without colour change in sulphuric acid and does not form a diazonium salt.

Ethyl acetoacetate forms "1-op-*dichlorophenyl*-3 : 4-*dimethyl*-1 : 2-*pyrazo*-6 : 7-*pyrone*" (annexed formula), which crystallises in yellow, rhombic leaflets, m. p. 223°. This is very stable towards acids or dilute alkalis, and, whilst chlorine does attack it, no diazonium salt is formed.
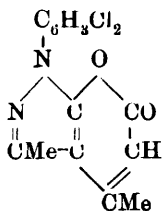
Acetone 2 : 4-*dichlorophenylhydrazone* is an unstable substance which crystallises in rhombs, m. p. 42°, b. p. 200°/100 mm., and is condensed by zinc chloride at 190° to 5 : 7-*dichloro*-2-*methylindole*. This forms large, highly refractive, rhombic crystals, m. p. 61°, and gives a deep violet-red coloration when a very minute trace is moistened with concentrated hydrochloric acid.

J. C. W.

Development of Colours Produced on the Plant Fibre with Diazotisable Dyes. AKTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P., 303409, 1917; from *Chem. Zentr.*, 1918, i, 495—496).—The dye, after diazotisation in the usual way, is developed by treatment with an *N*-alkyl derivative of chloro-*m*-phenylenediamine.

4-Chloro-*m*-phenylene-ethyldiamine, colourless crystals, m. p. 53°, can be obtained by nitrating *p*-chloroacetoethylanilide, followed by removal of the acetyl radicle and reduction of the remaining *p* - chloro - *m* - nitroethylaniline. 4 - Chloro-*m*-phenylenedimethyldiamine, colourless leaflets, m. p. 80°, is obtainable by nitrating *o*-chlorodimethylaniline and reducing the resultant nitro-compound.

D. F. T.

Globulin of Buckwheat, Fagopyrum fagopyrum. CARL O. JOHNS and LEWIS H. CHERNOFF (*J. Biol. Chem.*, 1918, **34**, 439—445).—The globulin of buckwheat has the following percentage composition: C 51·69, H 6·90, N 17·44, S 1·16, and O 22·81. It contains about 13% of arginine, 0·6% of histidine, 7·9% of lysine, and 1% of cystein, besides a small amount of tryptophan.

H. W. B.

Stizolobin, the Globulin of the Chinese Velvet Bean, Stizolobium niveum. CARL O. JOHNS and A. J. FINKS (*J. Biol. Chem.*, 1918, **34**, 429—438).—The new globulin, *stizolobin*, is the chief protein in the Chinese velvet bean. It has the following percentage composition: C 53·03, H 7·05, N 16·33, S 0·65, and O 22·94; and it contains about 1·15% of cystein, 6·7% of arginine, 2·4% of histidine, and 8·5% of lysine. Tryptophan is also present in stizolobin.   H. W. B.

The Swelling of Protein Colloids. LAURENCE J. HENDERSON and EDWIN J. COHN (*J. Amer. Chem. Soc.*, 1918, **40**, 857—861).— In reference to the investigations of Fischer and his co-workers (this vol., i, 129, 130, 131), it is stated that careful consideration of the experimental results fails to support the conclusions which have been drawn (see following abstract).   D. F. T.

The Colloidal–Chemical Theory of Water Absorption by Protoplasm. MARTIN H. FISCHER (*J. Amer. Chem. Soc.*, 1918, **40**, 862—867).—A reply to Henderson and Cohn (preceding abstract).   D. F. T.

Swelling of Protein Colloids. L. J. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 867—868).—A reply to Fischer (preceding abstract).   D. F. T.

Preparation of Strong Solutions of Hæmoglobin and of Colour Filters of Hæmoglobin Compounds. H. HARTRIDGE (*J. Physiol.*, 1917, **51**, 252—258).—Solutions of hæmoglobin containing up to 48% were obtained by dialysing centrifuged sheep's corpuscles in a collodion tube against flowing distilled water at 0° for a week or less in Dewar vessels. By mixing with warm gelatin solutions, colour filters of oxy- and carbonmonoxide-hæmoglobin were prepared, but they were not permanent.   G. B.

Hæmin Crystals and their Production. ZDZISLAW ZAWAL-KIEWICZ (*Pharm. Post.*, 1918, **51**, 45; from *Chem. Zentr.*, 1918, i, 540—541).—Teichmann's reaction is obtained most easily by placing a small quantity of the substance under examination on an objective glass with a drop of $N/10$-hydrochloric acid; this is then very carefully dried above a small flame, the residue moistened with 2—3 drops of concentrated acetic acid and a cover glass placed over the mixture. The mixture is again carefully warmed for about a minute, any acid lost by evaporation being replaced by another drop. When the end of the reaction is indicated by a reddish-brown colour, the remainder of the acid is allowed to evaporate, one or two drops of glycerol are introduced under the cover glass, and the characteristic crystals of hæmatin chloride are examined under the microscope. Ammonium chloride can be used satisfactorily in place of sodium chloride.   D. F. T.

Crystalline Nucleic Acids. S. J. THANNHAUSER and G. DORFMÜLLER (*Ber.*, 1918, **51**, 467—468).—Triphosphonucleic acid

(this vol., i, 47) has been partially hydrolysed to *cytidine-phosphoric acid*, $C_9H_{14}O_8N_3P$, rosettes of stout monoclinic-sphenoidal crystals, m. p. 227° (decomp.) (*di-brucine* salt, m. p. 180—182°), and *guanosine-adenosine-phosphoric acid*, $C_{20}H_{28}O_{15}N_{10}P_2$, stout, unsymmetrical triclinic crystals, m. p. 208° (decomp.) (*tetrabrucine* salt, m. p. 170°). Details of the process employed will be given in a subsequent, comprehensive communication.

J. C. W.

Stoicheiometrical Character of the Action of Normal Salts on the Swelling of Gelatin. JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 77—95. Compare this vol., i, 240; and Fenn, this vol., i, 318, 319).—The method previously described for the estimation of the effect of normal salts on the swelling of powdered gelatin has been applied to sodium gelatinate prepared by the action of $M/100$-sodium hydroxide, and to gelatin chloride prepared by the action of $M/100$-hydrochloric acid, on gelatin. It is found that the additional swelling of gelatin chloride is inhibited in solutions of normal salts with univalent cations and anions (type sodium chloride) in concentrations above $M/64$, and by salts with bivalent cations and univalent anions (type calcium chloride) in concentrations exactly half as high, namely, above $M/128$, no matter what the nature of cation or anion. Salts with bivalent anions (type sodium sulphate) have a limiting concentration of a much lower order, namely, $M/512$. In the case of sodium gelatinate, the limiting molecular concentration at which swelling is inhibited is twice as great for salts containing univalent anions and cations (such as sodium chloride) as for salts containing bivalent anions and univalent cations (such as sodium sulphate), whilst salts with bivalent cations (such as calcium chloride) have much lower limiting molecular concentration. Further, the additional swelling of gelatin, treated with $M/8$- or $M/4$-sodium chloride solution, is inhibited by normal salts in exactly the same way and at the same concentrations as sodium gelatinate. The normal salts, therefore, produce the same type of compounds with gelatin as the bases, namely, metal gelatinates which dissociate into a positive metal and a negative gelatin ion. These facts show that the limiting concentration of normal salts for the additional swelling is, within the restrictions mentioned, independent of the nature of the anion and cation of the salt, and this method could be used to calculate roughly the molecular concentration of the salt used.

When normal salts act on sodium gelatinate, apparently only the cation of the salt combines with the gelatin; and when normal salts react with gelatin chloride, only the anion will combine with gelatin, but not the cation. The experiments also show that gelatin salts with univalent anion or cation, such as gelatin chloride or sodium gelatinate, are capable of additional swelling, whilst salts of gelatin with bivalent ions are not. It is suggested that the swelling is due to electrolytic dissociation, which only occurs to a small extent in the case of gelatin salts with bivalent ions. It is evident that antagonistic salt action may be expected when

gelatin salts containing univalent ions are transformed into gelatin
salts with bivalent ions.   H. W. B.

**Influence of Normal Salts on the Viscosity of Gelatin
Solutions.** JACQUES LOEB (*J. Biol. Chem.*, 1918, **34**, 395—413.
Compare preceding abstract).—After gelatin has been treated with
$M/8$- or $M/16$-solutions of normal salts with univalent cations, and
the excess of salt then washed away, its viscosity is found to have
increased. The viscosity is estimated by dissolving an amount of
the treated gelatin, corresponding with 1 gram of the dry material,
in water and comparing the rate of outflow through a viscometer
at 24° with that of a solution containing 1 gram of washed gelatin
powder in the same volume (100 c.c.) of water. The effect on the
viscosity is stoicheiometrical, in so far that all normal salts with
univalent cations produce the same increase in the viscosity of
the gelatin solution, so long as the concentration of cation is the
same, regardless of the nature and valency of the anion. Salts
with bivalent cations do not produce any increase in the viscosity
of gelatin.

The action of salts on the viscosity of sodium gelatinate is
similar to that observed in the case of gelatin, but with gelatin
chloride (gelatin previously treated with $N/100$-hydrochloric acid)
salts with bivalent anions lower the viscosity of such treated gelatin,
salts with univalent anions have the opposite effect, whilst the
influence of the cations is imperceptible.

These results indicate that the viscosity of a gelatin solution is
influenced chiefly, if not exclusively, by only one of the two ions
of the normal salt, namely, the one with an electrical charge
opposite to that of the protein. Ordinary gelatin has acidic pro-
perties, and its viscosity is influenced, therefore, only by cations.
The same position is occupied by sodium gelatinate, but gelatin
chloride, yielding a positive gelatin ion, is affected only by anions.
Support is also afforded by these results to the hypothesis that
gelatinates with univalent cations are highly dissociable, whilst
those with bivalent cations are not.   H. W. B.

**Effects of Electrolysis on Gelatin and their Biological
Significance. III. Effects of Mixtures of Salts on the
Precipitation of Gelatin by Alcohol. Antagonism.** W. O.
FENN (*J. Biol. Chem.*, 1918, **34**, 141—160. Compare this vol.,
i, 240; and Loeb, preceding abstract).—By the method previously
described, it is shown that salts (like sodium chloride) with uni-
valent anions and cations decrease the effect of salts with bi- or
ter-valent anions or cations on the precipitability of gelatin by
alcohol, whilst salts with bi- or ter-valent cations antagonise those
with bi- or ter-valent anions. Small concentrations of salts with
bivalent cations (like calcium chloride) decrease the effect of sodium
chloride on gelatin, whilst small concentrations of salts with bi- or
ter-valent anions (like sodium sulphate) increase it. A pair of
salts with bivalent cations or a pair with univalent anions and
cations are not antagonistic in their effects.   H. W. B.

Effects of Electrolytes on Gelatin and their Biological Significance. IV. Precipitation of Gelatin by Mixtures of Salts. W. U. FENN (*J. Biol. Chem.*, 1918, **34**, 415—428. Compare preceding abstracts).—The effect of a mixture of salts on the precipitability of gelatin depends on the nature of the ions which are present. The experiments are performed by dissolving the gelatin in acid, alkali, or a normal salt, and estimating the amount of sodium chloride or sulphate which must be added in the solid form just to cause its precipitation. Acids, and salts in which the effect of the cation predominates, assist the precipitation of gelatin by sodium chloride, whilst alkalis, and salts with predominant anions, hinder it. When sodium sulphate is substituted for sodium chloride, the precipitation of the gelatin is hindered by small, and assisted by higher, concentrations of alkali. H. W. B.

The Variability in the Activity of Ptyalin. F. DE BRUYNE (*Arch. néerland. physiol.*, 1918, **2**, 358—363).—Some observations indicating a periodicity in the activity of ptyalin when kept at 35°. S. B. S.

Physiological Chemistry.

Respiratory Metabolism and the Question as to the Formation of Sugar from Proteins and their Degradation Products. JOSÉ M. DE CORRAL (*Biochem. Zeitsch.*, 1918, **86,** 176—222).—It has been shown that the administration of Witte's peptone to a dog renders the liver practically free from glycogen. The effect of this administration on the respiratory quotient has been investigated, and also the effect of adding protein and amino-acid diets after peptone treatment. The Jacquet apparatus was employed for measurement of the gaseous exchanges. After eight days' starvation, the respiratory quotient for dogs sinks to 0·682, which is less than that after ingestion of fat. Practically the same low respiratory quotient is obtained after an interval of some hours after the last treatment, when the animal has had Witte's peptone administered to it for two days. When a carbohydrate diet is given, it is possible to determine the formation of glycogen by ascertaining the respiratory quotient seventeen or eighteen hours after the last ingestion. That the capacity for forming glycogen from carbohydrates after administration of peptone is diminished can be ascertained, even after an interval of twenty-four hours. But although diminished, it still exists, as is shown by comparing the value of the respiratory quotient with that obtained after administration of carbohydrates during starvation. If fats exclusively are administered after two days' treatment with peptone, the respiratory quotient *in a following period*

of starvation is the same as that after peptone action. If, after peptone treatment, amino-acids or proteins are administered, carbohydrates are formed, for the respiratory quotient in the following period of starvation indicates combustion of carbohydrates. Such a formation of carbohydrates from amino-acids or meat only appears to take place, however, when carbohydrates are wanting in the organism.   S. B. S.

The Wanderings of the Ions in Serum and Blood under the Influence of Carbon Dioxide, Acid, and Alkali. H. J. HAMBURGER (*Biochem. Zeitsch.*, 1918, **86**, 309—324).—The author, using an ultra-filtration method, is able to confirm the statement of Rona and György, that when carbon dioxide acts on the serum, the chlorine passes into a non-diffusible form, by combining with the proteins. The same happens after addition to the serum of very small amounts of sulphuric acid and of larger amounts of acetic acid. SO_4 also passes into a non-diffusible form after treatment of the serum with hydrochloric acid. When carbon dioxide acts on blood, it is possible to ascertain that not only does SO_4 attach itself in non-diffusible form to the serum proteins, but that it also goes into the corpuscles. The same phenomena take place after addition to blood of minute amounts of hydrochloric acid. The reverse effect to that produced by acids is observed after addition of small amounts of potassium hydroxide, in that Cl and SO_4 are set free from combination with the proteins and pass into a diffusible form.   S. B. S.

Can the Amount of Combination of Carbon Dioxide with Blood-serum be regarded as a Measure of the Reaction of the Blood ? K. A. HASSELBALCH and E. J. WARBURG (*Biochem. Zeitsch.*, 1918, **86**, 410—420).—The carbon dioxide tension, under which the blood is centrifuged for separation of the serum, is of great influence. By high carbon dioxide tension during centrifugalisation, the curve representing the relationship between carbon dioxide tension and carbon dioxide bound to the serum is shifted upwards, whereas by lower tension during centrifugalisation, it is shifted downwards. For this reason, it is not possible to draw correct conclusions as to acidosis and the reaction of the blood by measuring the capacity of the serum to combine with carbon dioxide, unless account is taken of the tension of the carbon dioxide prevailing during the preparation of the serum from the blood. It may be recalled that the carbon dioxide tension influences also the distribution of Cl' and other ions between the serum and corpuscles (Hamburger).   S. B. S.

The Presence of Phosphates in Human Blood-serum. V. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **86**, 395—409. Compare A., 1917, i, 520; this vol., i, 50, 203).—An analysis of the various forms of phosphorus in the serum in six pathological cases.
     S. B. S.

The Presence of Invertase in Serum. G. H. BOISSEVAIN (*Arch. néerland. physiol.*, 1918, **2**, 415—419).—The discordant results of various observers as regards the presence of invertase in the serum after injection of sucrose are discussed. It is shown that the leucocytes contain invertase, and it is suggested that the presence in the serum after injection of various sugars in solution is due to the injury of the leucocytes and the setting free of the ferment; in fact, an invertase can be detected in the serum after injection of water, or the formation of a clot in the veins by introduction of a silk thread. The leucocytes used in the experiments were obtained from an aseptic abscess produced by terebenthene. S. B. S.

Antigens. XII. The Relationship between Serological Specificity and Chemical Structure. (Preparation of Antigens with Specific Groups of known Chemical Structures). KARL LANDSTEINER and HANS LAMPL (*Biochem. Zeitsch.*, 1918, **86**, 343—394).—A series of antigens was made by combining horse serum with the diazo-derivatives obtained from the following "azo-components": aniline, *o-*, *m-*, and *p*-aminobenzoic acids, *o-*, *m-*, and *p*-aminobenzenesulphonic acids, *p*-aminophenylarsinic acid, and a number of chloro-, bromo-, and nitro-*o*-substitution products of these substances, *o-*, *m-*, and *p*-aminocinnamic acids, naphthionic acid, and aminoazobenzenedisulphonic acid. The method of preparing solutions containing serum proteins coupled with these various diazo-derivatives is described. The antigens were then injected into rabbits until active immune sera were obtained. The precipitin reaction of the various immune sera towards native horse sera differed. The reaction of the immune sera towards the various antigens (diazo-proteins) prepared from horse serum, egg-albumin, and in a few cases edestin, was also investigated. Altogether 23 kinds of immune sera were prepared, and their action on 33 azoproteins was investigated. Of these, only 6 were completely specific, acting only on the homologous antigens containing the same azo-components. Of the antigens, 15 acted only with one immune serum. The other immune sera and antigens showed a broader sphere of action. The results are tabulated by the author, who summarises the relationship of the various antigens to one another and the relationship of the chemical structure of the azo-components and serological action. The possibility of distinguishing chemical groups by serological reactions is suggested. S. B. S.

Calcium and Magnesium Metabolism. IV. Experiments on Man. MAURICE H. GIVENS (*J. Biol. Chem.*, 1918, **34**, 119—130. Compare A., 1917, i, 603).—The daily urinary excretion of calcium and magnesium of nine healthy adults on a diet of natural foods containing more magnesium than calcium ranged from 0·05 to 0·24 gram of calcium and from 0·03 to 0·15 gram of magnesium, whilst on a diet having more calcium than magnesium the limits

were 0·12 to 0·47 gram of calcium and 0·05 to 0·23 gram of magnesium. In general, although not always, more calcium than magnesium is excreted in the urine. The urinary output of both calcium and magnesium is increased by consumption of milk; calcium lactate always increases the urinary excretion of calcium, although not to such an extent as is effected by milk; magnesium lactate does not seem to produce any greater elimination of magnesium in the urine. The results obtained do not allow of any simple relationship being established between urinary excretion of calcium and body-weight.   H. W. B.

Carbohydrate Metabolism. I. Elimination of Sugar in the Urine of the Normal Dog. STANLEY R. BENEDICT and EMIL OSTERBERG [with CECIL DUDLEY] (*J. Biol. Chem.*, 1918, **34**, 209—216).—By means of a new method for estimating traces of sugar in urine (this vol., ii, 247), the authors are able to record the changes in the hourly excretion of sugar by a normal dog. The amount of sugar eliminated is independent of the volume of urine secreted. The percentage of sugar varies greatly; in one dog it ranged from 0·021 to 0·36%. The amount of sugar excreted per hour gradually rises after a meal, reaches a maximum in about five hours, and then falls to normal. The urine almost invariably contains some kind of sugar, but occasionally during the periods of minimum elimination, fermentable sugar (dextrose) disappears entirely from the urine. During the period of maximum sugar elimination, the reaction of the urine approaches neutrality, and in some cases becomes alkaline to litmus. The twenty-four hours' sample was invariably acid. The discussion of the bearing of these points on views as to carbohydrate metabolism is reserved for a future paper.   H. W. B.

Carbohydrate Metabolism. II. Urinary Sugar Excretion in Two Normal Men. STANLEY R. BENEDICT, EMIL OSTERBERG, and ISAAC NEUWIRTH (*J. Biol. Chem.*, 1918, **34**, 217—262. Compare preceding abstract).—The results show that sugar is always present in normal human urine. Feeding with either meat or a carbohydrate diet causes an increase in the elimination of sugar. Glycosuria is therefore a physiological condition, and the normal organism can be said to be diabetic. The authors propose to abandon the use of the word " glycosuria," and suggest the term " glycuresis " to denote an increase of sugar in the urine. Glycuresis occurs after the ingestion of food, the percentage of sugar in the urine rising after a meal from about 0·05 to 0·3 or sometimes to as much as 0·6. A certain degree of tolerance for dextrose is shown in that, after the ingestion of 20 to 50 grams of dextrose, the resulting glycuresis is not greater than is observed after an ordinary meal. Yet the addition of 20 grams of dextrose to an ordinary meal may lead to a relatively great output of sugar in the urine, indicating a profound disturbance in carbohydrate metabolism. The total amount of sugar eliminated in the urine by a normal person is about 1 to 1·5 grams daily. and in persons

with a tendency to diabetes this maximum is not only exceeded, but the ratio of unfermentable to fermentable sugar in the urine becomes changed. H. W. B.

Inorganic Elements in Nutrition. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 131—140).—Full description of work previously published (this vol., i, 277). H. W. B.

Nutritive Factors in Animal Tissues. II. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 17—27. Compare this vol., i, 140).—Besides the liver, the heart, kidney, or brain of the pig contains sufficient water-soluble vitamine to effect rapid growth in the rat when constituting the sole source of protein and water-soluble vitamine in the food. In some cases, normal growth occurs also without the addition of any source of fat-soluble vitamine other than that contained in the tissue itself. These tissues are therefore better foods than dried beef (compare Cooper, A., 1914, i, 777, and Osborne and Mendel, *loc. cit.*). They can be dried and heated for several hours at 90° without any loss of water-soluble vitamine occurring. The oil expressed from liver tissue is rich in fat-soluble vitamine, and it effectively cures or prevents the nutritive decline and the pathological manifestations which are the characteristic outcome of feeding with a diet otherwise devoid of fat-soluble vitamine. H. W. B.

The Nature of the Constituent of Intestinal Extracts which Exerts a Stimulating Influence on the Gastrointestinal Movements. J. W. LE HEUX (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 805—811).—The presence of this constituent was first demonstrated by Wieland. The author describes experiments for its isolation, and draws the conclusion that it is most probably choline. Its physiological activity is markedly increased by acetylation. S. B. S.

Quantity of Metal Fixed by Organic Extracts and Proteins. II. Catalytic Power of Egg-albumin treated with Metallic Powders. S. REBELLO-ALVES and A. BENEDICENTI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 79—96, 150—156; from *Physiol. Abstr.*, 1918, **3**, 100).—Powdered copper and cobalt are fixed in varying proportions by different organs; liver, owing to its more rapid autolysis, fixes most.

The catalytic power of egg-albumin towards hydrogen peroxide is not increased by heating it with powered quartz, but is increased five or six times by cobalt powder. Nickel, iron, and copper do not increase catalysis, and lead and antimony diminish it. S. B. S.

Suprarenal Glands in Relation to Carbohydrate Metabolism. I. Influence of Repetition of Adrenaline Injection on the Intensity of Glycosuria and Hyperglycæmia and the Glycogen Content of the Liver. II. Influence of Adrenalectomy on the Glycogenetic Power of the Liver. III. Adrenaline Content of the Suprarenal Glands in Various Experimental Conditions. SHIGENOBŪ KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 269—285, 287—297, 299—319).—Daily repetition of subcutaneous injection of adrenaline is followed on each occasion by the excretion of about the same .quantity of sugar in the urine so long as the animals (rabbits) are well fed.. When the animals are allowed to fast, the daily sugar excretion rapidly diminishes until only ˙a slight glycosuria is produced. The hyperglycæmia produced by daily adrenaline injections remains practically constant, no matter whether the animal is fasting or well fed. The reason of the failure of the hyperglycæmia caused by the injection of adrenaline into fasting animals to produce the typical glycosuria is not elucidated. Injection of adrenaline into fasting rabbits leads to a storage of glycogen in the liver. A combination of fasting and adrenaline injections does not therefore render the liver of an animal free from glycogen.

Rats after adrenalectomy still retain the power to form glycogen from carbohydrates in the liver; adrenaline does not exert a controlling action on the glycogenetic function of the liver.

The amount of adrenaline in the suprarenal gland after removal from the body gradually diminishes unless the gland is kept in an oxygen-free medium. The adrenaline content of the gland in the living rabbit is not altered by fasting, by repeated injections of adrenaline, or by injection of a single large dose of this substance. Removal of one gland is partly compensated for by growth of the companion gland, resulting in an increase in the absolute amount of adrenaline in the gland, although, owing to the relatively greater growth of the glandular tissue, the percentage of adrenaline in the companion gland is reduced.   H. W. B.

Estimation of Various Forms of Nitrogen in Raw Beef, including the Products of Hydrolysis of some of the Proteins. I. Hexone Bases of some Proteins of Beef. II. Bromination of the Hydrolysates of some Proteins of Beef. WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **34**, 343—353, 355—362. Compare Trowbridge and Grindley, A., 1906, ii, 374).—The proteins of beef which are insoluble in cold water, yield on hydrolysis less humin, ammonia, histidine, and more arginine nitrogen than the coagulated water-soluble proteins. Since the former represent the stroma and the latter the plasma of the muscle fibres, it appears that these components of the cell are composed of essentially different proteins. The comparison of the analyses of the muscular tissues of a new-born calf and of a five-year-old steer indicates that during growth the insoluble proteins probably change in composition.

A method is described for estimating histidine in proteins by

hydrolysis followed by bromination. After deducting the amount of bromine absorbed by cysteine and allowing for the solubility of histidine in phosphotungstic acid, figures are obtained which tally closely with those afforded by Van Slyke's method (A., 1911, ii, 944). Under the conditions described, a molecule of cysteine absorbs about ten atoms of bromine, whilst a molecule of histidine absorbs two.　　　　　　　　　　　　　　　H. W. B.

The Skin Secretion of Frogs. FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1917, **81**, 319—382).—The secretion is best obtained by electrical stimulation of washed frogs, and consists of coagulable protein, mucin, albumoses, peptones, amino-acids (7% of leucine), purine bases, cholesterol and its esters. The dried secretion kills tadpoles and small fishes in a 1 : 80,000 solution ; 6—12 mg. per kilo. intravenously kills rabbits. The dried secretion has a strong local irritant action on the skin ; the active substance resembles the saponins in its chemical and pharmacological properties, and is quite distinct from the heart poison of the toad's skin. It could not be obtained pure, but gives Liebermann's cholesterol reaction and seems to be a lactone.　　　　　　　　　　　　　G. B.

The Excretion of Saponins in the Urine, and their Action on the Blood after Internal Administration. JOSEF FIEGER (*Biochem. Zeitsch.*, 1918. **86**, 244—297). Sapindus saponin, after administration to dogs, is partly excreted in the unchanged form in the urine, and can be detected by its hæmolytic action. The sapogenin can also be isolated from the urine after hydrolysis with sulphuric acid ; this substance exerts also a hæmolytic action. The detection of the guaiacum saponin in the urine is most difficult, as it is not hæmolytic. The author shows, however, that it yields on hydrolysis two sapogenins, the mixture of which is strongly hæmolytic. The urine of an animal to which the saponin had been administered is not hæmolytic, but it exerts a hæmolytic action after hydrolysis. The saponin is therefore excreted in the urine unchanged. In an experiment with quillaja saponin, this substance could not be detected in the urine; in this case, however, the experiment had been carried out on an animal to which other saponins had been previously administered, and reasons are given for supposing the animal had acquired a general tolerance to the group of saponins, and had degraded the quillaja saponin in the intestine, excreting the sapogenin in the fæces. In the case of a second dog to which the saponin was administered, small amounts were found in the urine. In the case of all three saponins. a marked excretion of bile pigments in the blood took place, which is taken as evidence of the resorption of these substances. They also exerted a temporary diuretic action.　　　　　　　S. B. S.

The Excretion of Saponin in the Fæces. HANS BÄCK (*Biochem. Zeitsch.*, 1918, **86**, 223—242).—Sapindus and quillaja saponins were administered to hens and dogs. They cause irritation of the alimentary tract, and undergo hydrolysis either by

enzymes or by microbes. The sapogenins are excreted with the fæces, and their presence was detected by their hæmolytic action on the corpuscles of various species. From the sapindus saponin apparently two sapogenins are obtained in the fæces, one of which is soluble in ethyl acetate and is strongly hæmolytic, whilst the other is insoluble and not hæmolytic. From quillaja saponin, two sapogenins also appear to be formed, one soluble in ethyl acetate and strongly hæmolytic, the other insoluble in this reagent, but weakly hæmolytic. S. B. S.

Cæsium Ions and Cardiac Action. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam,* 1918, **20**, 773—778).—The light radioactive metals and the allied cæsium, as well as the heavy radioactive metals uranium, thorium, niton, and radium, sustain the contractility of the isolated frog's heart when the ventricle is pulsating on its own activity. The author gives the effectual doses of these for summer frogs. There is a biological antagonism between potassium, cæsium, and rubidium, on the one hand, and uranium, thorium emanation, and niton, on the other. Probably cæsium emits β-rays of low penetrating power on which its effect, similar to that of potassium and rubidium, depends. S. B. S.

Distribution and Elimination of Zinc and Tin in the Body. WILLIAM SALANT, J. B. RIEGER, and E. L. P. TREUTHARDT (*J. Biol. Chem.,* 1918, **34**, 463—470).—After the administration of zinc salts to cats or rabbits by the mouth, or by subcutaneous or intravenous injections, the metal is eliminated almost entirely in the fæces. Tin salts are similarly dealt with, except that a significant proportion passes off in the urine. Storage of both metals occurs in the liver, skin, and bones. H. W. B.

Production of Glycosuria by Zinc Salts. WILLIAM SALANT and LOUIS ELSBERG WISE (*J. Biol. Chem.,* 1918, **34**, 447—462).—The intravenous injection of zinc malate into rabbits produces slight hyperglycæmia and glycosuria. Glycosuria is also caused by subcutaneous injections and by the administration of the zinc malate or acetate with the food, but much larger doses are required. The amount of sugar in the urine after the injection usually reaches about 0·35 per cent. Albuminuria accompanies the glycosuria and is sometimes very marked. H. W. B.

Dichloroethylene as a Narcotic. HERMANN WITTGENSTEIN (*Arch. exp. Path. Pharm.,* 1918, **83**, 235—247).—An atmosphere containing about 1% by volume of dichloroethylene causes deep narcosis in various mammals, but, unlike chloroform, it does not depress the heart and blood vessels. It has been successfully tried on man in a few cases. G. B.

The Taking up of Ethyl Alcohol by the Lungs. A. LOEWY and R. VON DER HEIDE (*Biochem. Zeitsch.,* 1918, **86**, 125—175).—A detailed investigation of the amounts of ethyl alcohol taken up

from the air by rats and guinea-pigs and of the amounts remaining in the bodies and burnt. As compared with methyl alcohol, the amounts of ethyl alcohol stored in the body are small. The amount stored per millimetre tension of alcohol vapour in the air is smaller the greater the tension. The combustion of ethyl alcohol is greater than that of methyl alcohol, and this accounts for the greater quantities of the latter found stored in the body. The conclusion is drawn that ethyl alcohol is, generally, more toxic than methyl alcohol. A few experiments on man are also described.

S. B. S.

Gossypol, the Toxic Substance in Cotton Seed. W. A. WITHERS and FRANK E. CARRUTH (*J. Agric. Research*, 1918, **12**, 83—102. Compare Carruth, this vol., i, 266).—Cotton-seed meal is much less toxic than raw cotton seed, probably owing to the oxidation of gossypol during cooking. Feeding experiments with rats, rabbits, and pigs are described, details of which are given in *J. Soc. Chem. Ind.*, 1918, 164A.

W. G.

Metabolic Changes Induced by Administration of Guanidine Bases. II. Influence of Guanidine on Urinary Ammonia and Acid Excretion. III. Relation between the Tetanoid Symptoms of Guanidine Administration and the Condition of Acidosis. IV. Influence of the Administration of Calcium on the Sugar Content of the Blood in Rabbits with Guanidine Hypoglycæmia. C. K. WATANABE (*J. Biol. Chem.*, 1918, **34**, 51—63, 65—72, 73—76. Compare this vol., i, 205).—The subcutaneous injection of guanidine hydrochloride into a rabbit is followed immediately by a diminished excretion of nitrogen in the urine. The ammonia eliminated in the urine is increased, however, so that the ratio, ammonia/total nitrogen, is greatly increased. There is a fall in the hydrogen ion concentration, and the urine may become neutral or alkaline.

The effect of the injection on the blood is to produce a marked increase in its hydrogen ion concentration and a corresponding decrease in the alkaline reserve, specially noticeable after the manifestation of the symptoms of tetany. It appears, therefore, that the excretion of the excess of ammonia in the urine in tetany is the result of the operation of a protective mechanism by means of which the liver seeks to neutralise the acid produced by the excessive muscular activity (compare Carlson and Jacobson, A., 1910, ii, 324).

All the toxic symptoms following parathyroidectomy are paralleled by those produced by the injection of guanidine into the system. The hypoglycæmia manifested after thyreoparathyroidectomy is also produced by the administration of guanidine (*loc. cit.*), but it is now shown that neither the tetany nor the hypoglycæmia resulting from guanidine injections can be removed by treatment with calcium lactate, which has been shown to abolish these symptoms when produced by operative procedures (compare Underhill and Blatherwick, A., 1914, i, 1184).

H. W. B.

The Fate of Quinine in the Organism. HEINZ HARTMANN and LORO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).— A gravimetric method of estimation in urine is described (precipitation as tannate, decomposition of the latter, extraction from water with ether), and a method, based on the fluorescence, for estimation in blood (compare Ramsden and Lipkin, this vol.. ii, 251). At most, 40% of administered quinine is excreted in urine and fæces; the rest is not deposited in the organs, and must therefore have been destroyed. After intravenous injection, the amount in the blood sinks rapidly, then more slowly, to zero (eight hours after 0·5 gram), but oral administration gives a lower, more constant quinine level, which is retained for about twenty-four hours.   G. B.

Physiological Behaviour of Raffinose. II. SHIGENOBU KURIYAMA (*J. Biol. Chem.*, 1918, **34**, 321—333. Compare Kuriyama and Mendel, A., 1917, i, 611).—Raffinase is present in mung bean (*Phaseolus aureus*), cotton seed, and soja bean. It can also be extracted from rabbits' fæces. Raffinase (from yeast) is readily destroyed by the gastric juice, but when yeast is fed to an animal, a portion of the raffinase escapes destruction and passes into the excreta.   H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

The Formation of Ferments. VI. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **86**, 329—336. Compare A., 1917, i, 305, 430, 528). —Leucine promotes the urease fermentation in the case of *Bacillus coli*, but it inhibits the sugar-fermenting action of the same bacterium. The significance of certain fragments of the protein molecule for the formation of ferments, and the general physiological significance of proteins for growth, are discussed by the author. S. B. S.

Influence of Nitrates on Nitrogen-assimilating Bacteria. T. L. HILLS (*J. Agric. Research*, 1918, **12**, 183—230).—A great increase in the number of azotobacter in sterilised soil was produced by the application of small quantities (up to 0·1%) of potassium, sodium, or calcium nitrate, but ammonium nitrate was much less effective, and higher concentrations of all the nitrates were not so favourable to the growth of the organism. There was also an increase in the total nitrogen in the soil, but this increase was not commensurate with the increase in the number of azotobacter present. On agar films, the results were somewhat different, calcium nitrate causing a decrease in the amount of nitrogen fixed.

All three nitrates caused an increase in the number and size of the volutin bodies in the azotobacter cells and a marked pigmentation. The number of *Bacillus radicicola* in sterilised soil was increased by the application of small quantities of the three nitrates, and, although this increase was less marked than in the case of azotobacter, the *B. radicicola* appeared to be more resistant to higher nitrate concentrations. Unlike the azotobacter, *B. radicicola* does not reduce nitrate to nitrite under aerobic conditions. The presence of large amounts of potassium, sodium, and calcium nitrates proved detrimental to the formation of nodules on alfalfa.

W. G.

Presence of a Growth-producing Substance in Cultures of Typhoid Bacilli. August J. P. Pacini and Dorothy Wright Russell (*J. Biol. Chem.*, 1918, **34**, 43—49).—It has long been recognised that in certain infectious diseases growth is induced, apparently, by the infection. In typhoid fever, for example, the patient may grow from one to even several inches in height. It is now shown that the fat- and protein-free extract of typhoid bacilli contains a vitamine which when added to the food causes rapid growth of rats on a diet on which otherwise they gradually lose weight and die. The extract gives the blue coloration with Folin's uric acid reagent, which is given by vitamine-containing extracts prepared from yeast and other sources. The authors indicate the bearing of these results on the question of a more scientific method of feeding in these cases.   H. W. B.

The Preparation of Phosphoric Acid Esters of Carbohydrates (Zymophosphate) by Living Yeasts. Hans Euler (*Biochem. Zeitsch.*, 1918, **86**, 337—342).—Neuberg has found that yeast in presence of toluene could only bring about an esterification of 7—8% of added phosphate, whereas the author found that it could bring about a complete conversion into the ester. Attention is now directed to the facts (*a*) that excess of toluene acts toxically and inhibits the zymophosphate formation, although small amounts are necessary to bring this about, and (*b*) not all yeasts are capable of zymophosphate formation; two out of eleven bottom beer yeasts investigated by the author gave negative results. The author confirms Harden and Young in showing that dihydroxyacetone can only give rise to a small amount of zymophosphate.   S. B. S.

The Influence which the Plant Function of Yeast Exercises on the Yield of Alcohol; new Interpretation of Ferment Power. L. Lindet (*Compt. rend.*, 1918, **166**, 910—913).—An examination of the relative effects of the plant function and the zymase function of yeast during alcoholic fermentation. The author has studied the effect of varying the nutritive value of the bouillon, the concentration of the sugar solution, the vigour of the yeast, the temperature, the thickness of sowing, and the origin of the yeast on the yield of alcohol. The ferment power

must be considered as the sum of the plant power, tending to consumption of sugar, and the zymase power producing the alcohol. These two powers are higher as the crop of yeast is less abundant and the fermentation is prolonged. Except in the case of temperature variation, the weight of sugar utilised to produce a given weight of yeast is independent of the conditions. [See, further, *J. Soc. Chem. Ind.*, July.]   W. G.

Precipitation of Proteins by Narcotics. OTTO MEYERHOF (*Biochem. Zeitsch.*, 1918, **86**, 325—328).—Freundlich and Rona (A., 1917, ii, 365) have explained the sensitisation of colloids to precipitating salts by the action of narcotics. The same explanation applies to the following phenomena, observed with Lebedev's maceration juice of yeast. The original juice is readily precipitated on addition of 6% ethyl urethane. The residue from ultrafiltration is not so precipitated, but precipitation readily takes place when the ultra-filtrate is added to it. The combined action of salts and narcotics is necessary for precipitation.   S. B. S.

Growth of Aspergillus glaucus under the influence of Large Quantities of Potassium Nitrate. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**, 599—602).—A series of tables indicating the marked influence exerted by potassium nitrate on the rapidity of growth of *Aspergillus glaucus*.   A. J. W.

Acids Produced by Mucor Boulard. BETTINGER and DELAVALLE (*Bull. Assoc. Chim. Sucr. Dest.*, 1917, **35**, 13—15. Compare *J. Soc. Chem. Ind.*, 1918, 219A, 345A).—*Mucor Boulard* (employed industrially for the saccharification of distillery mashes), cultivated in sugared extract of malt-combs, yields succinic acid as sole non-volatile acid, and a much smaller proportion of acetic acid. The production of acid is favoured by aeration, high sugar-content of the medium, and relatively low temperatures of culture. Ether extracts about 21% of the dry substance of the plant grown under these conditions.   J. H. L.

The Formation of Soluble Starch by Moulds and the Question of the Synthesis of Proteins by these Organisms. FRIEDRICH BOAS (*Biochem. Zeitsch.*, 1918, **86**, 110—124).—In continuation of his investigations on the formation of soluble starch (A., 1917, i, 370, 503), the author now shows that quinic acid can serve as a source of carbon. In presence of asparagine, the percentage of the acid must be more than 6%, but in the presence of ammonium sulphate, 3·6% of quinic acid is sufficient, as acid is necessary for the process, and in the latter case it is set free from the ammonium sulphate. The author criticises some earlier work dealing with the utilisation of various nitrogenous substances by plants, especially that of Czapek, Brenner, and Puriewitsch. He shows that certain factors have been left out of account in drawing conclusions from experimental results. More especially, he shows

that the acidity of the medium is to be taken into account, which may be due to the acid derived from the salts. His own experiments on the formation of soluble starch require the presence of acid. Furthermore, in estimating the yield of the moulds, no account has been taken of proteoclastic action, in that a mould may grow, and after a time the amount will diminish owing to this action. This factor again is influenced by the presence of acids.   S. B. S.

•Basis of Measurement of Antagonism. W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **34**, 363—368).—A theoretical paper in which the possible methods of measuring the antagonistic action of salts on the growth of plants and animals is discussed.

                                                                                                H. W. B.

The Relation of some of the Rarer Elements in Soils and Plants. W. O. ROBINSON, L. A. STEINKOENIG, and C. F. MILLER (*U.S. Dept. Agr., Bull.*, 1917, No. 600; from *Physiol. Abstr.*, 1918, **3**, 75).—About fifty samples of legumes, grasses, vegetables, trees, and shrubs grown on nine soils of known composition, or obtained from localities where certain rare elements were known to occur, were examined. Lithium was found in spectroscopic traces in all the plants examined (max. 0·00015%). Rubidium was found in most cases and in larger quantities than the other rare alkalis (max. 0·025%), and in the cases where the amount of rubidium oxide exceeded 0·01% in the plant, minerals containing this element were known to occur in the soil. Cæsium was found in only three plants obtained from a locality where cæsium beryls occur. Chromium was occasionally found, although always in small quantities. Vanadium was only detected in six cases, and then in traces. Molybdenum was not found. Barium was found in all samples and strontium in all but one, and titanium occurred in minute quantities in all samples. With two exceptions, all the plants contained aluminium, the percentage in pine needles being exceptionally high (max. 0·253%). Methods of analysis are given in an appendix.   W. G.

Flavone Derivatives in Plants. III. Tropical Plants. K. SHIBATA and I. NAGAI (*Bot. Mag., Tokyo*, 1916, **30**, 149—178; from *Physiol. Abstr.*, 1918, **3**, 68—69).—The leaves, sprouts, blossoms, bark, and wood of two hundred and forty-two species were examined, and it was found that flavones were invariably present. The flavone glucosides of the cell sap exert a protective action against the solar rays, especially those of short wave-length. Thus plants grown under glass for some time contained less flavone than those grown in the open, and those grown in the shade less than those grown in the sun. Plants provided with a heavy cuticular layer were usually poor in flavones. The function of the flavone in the cell sap of the plants is similar to that of the pigment of the human skin. Flavone and anthocyanin often inter-

change. Thus young sprouts frequently contain anthocyanin-red, which changes into the colourless flavone glucoside in the grown organ, and back again into anthocyanin before the fall of the leaves. The winter buds of many plants contain flavones both in the tissues of the lower leaves and the viscous exudate. In many cases, the wax-like or powdery covering of the plant organs contains flavone compounds secreted by the epidermis [compare Müller, T., 1915, **107**, 872]. W. G.

Some Constituents of the American Grapefruit (Citrus decumana). HARPER F. ZOLLER (*J. Ind. Eng. Chem.*, 1918, **10**, 364—374).—Analyses of grapefruit showed that the peel contained 2·5 to 6·0 grams per fruit of essential oils, principally *d*-limonene (90—92%), with small quantities of citral, α-pinene, geraniol, and linalool ; also about 0·2 to 1·6 grams of the glucoside naringin per fruit and about 4 grams of pectin. The pulp contains about 1·9 to 6·0 grams of citric acid, 6·2 to 15 grams of sucrose, and 8·6 to 19·6 grams of dextrose per fruit. [See, further, *J. Soc. Chem. Ind.*, 387A.] W. F. F.

A New Compound in Hyssop Killed by Fungus. O. TUNMANN (*Pharm. Post*, 1917, **50**, 773—774; from *Chem. Zentr.*, 1918, i, 29—30).—The cells of some hyssop plants which had been killed by moulds were found to contain as the chief crystalline deposit a colourless substance which has m. p. 275°, yields protocatechuic acid on fusion with potassium hydroxide, and is probably a flavone derivative. It is designated *hyssopin*, and resembles, but is not identical with, hesperidin, which has already been found in unusually large quantity in mint killed by fungus.
J. C. W.

Non-protein Nitrogen of Wheat Flour. M. J. BLISH (*J. Biol. Chem.*, 1918, **33**, 551—559).—The proteins are precipitated from an aqueous extract of wheat flour by treatment first with $N/10$-sodium hydroxide and then with $N/10$-copper sulphate solution, the non-protein nitrogen being subsequently estimated in the filtrate. Wheat flour contains 2 mg. of amino-acid nitrogen and 6 mg. of amide nitrogen per 100 grams of flour, as well as a considerable amount of non-protein nitrogen in an unknown form. [See also *J. Soc. Chem. Ind.*, 279A.] H. W. B.

Boron. Its Effects on Crops and its Distribution in Plants and Soils in Various Parts of the United States. F. C. COOK and J. B. WILSON (*Proc. Amer. Soc. Biol. Chem.*, 1917, vi—vii; *J. Biol. Chem.*, 1918, **33**).—Boron in the form of borax or colemanite (calcium borate) is an effective larvicide for the housefly; care must be exercised in the subsequent distribution of manure to which it has been added, because small percentages of boron in some soils are found to exert a toxic action on certain plants, especially the *Leguminosae*. [See also *J. Soc. Chem. Ind.*, 274A.] H. W. B.

Organic Chemistry.

Oxidation Products of Paraffin Wax. AKTIEN-GESELLSCHAFT FÜR MINERALÖL-INDUSTRIE VORM. FANTO & Co. (*Zeitsch. angew. Chem.*, 1918, **31**, i, 115).—The method of oxidising paraffin wax by means of atmospheric oxygen was not discovered by Bergmann as he suggests (this vol., i, 285), but by Freund in 1915.

C. A. M.

Besson's Method for the Preparation of Chloroform from Ethyl Alcohol. K. UKITA (*J. Chem. Ind., Tokyo*, 1918, **21**, 219—216).—A stream of chlorine gas is passed into 100 grams of alcohol until the product has D 1·299, when it is added to a mixture of 500 grams of bleaching powder, 100 grams of milk of lime, and 2 litres of water, and the liquid is distilled. The yield is 95—98 grams of chloroform. During the treatment of the alcohol with chlorine, the liquid separates into two layers; the heavy layer increases gradually, and when the chlorination is satisfactory the liquid again becomes homogeneous. J. F. B.

Some Fluoro-bromo-compounds of the Methane and Ethane Series. HANS RATHSBURG (*Ber.*, 1918, **51**, 669—672).—Completely brominated compounds react with silver fluoride to form fluoro-bromo-derivatives. Thus, carbon tetrabromide and silver fluoride in the molecular proportion 1 : 2 react at above 50—60° to form *fluorotribromomethane*, CBr_3F, as a colourless, heavy, pleasant-smelling liquid, b. p. 107°/760 mm., which is insoluble in water. This reacts with more silver fluoride, best at 140—150°, giving *difluorodibromomethane*, a mobile, readily soluble liquid, b. p. 24·5°/760 mm., m. p. below −80°. Ethyl tribromoacetate and silver fluoride (1 : 4) react at 190—200° to give *ethyl fluorodibromoacetate*, an insoluble liquid, b. p. 171—173°/760 mm., which is very readily hydrolysed. J. C. W.

Inhibitory Effects of Water on the Interaction of Aluminium and (*a*) **the Fatty Acids ;** (*b*) **Phenol, Cresol, and** α- **and** β-**Naphthols ;** (*c*) **Methyl, Ethyl, Butyl, Amyl, and Benzyl Alcohols.** RICHARD SELIGMAN and PERCY WILLIAMS (*J. Soc. Chem. Ind.*, 1918, **37**, 159—164. Compare A., 1916, ii, 187).—A continuation of work previously recorded. It is definitely shown that when dry fatty acids, dry alcohols, and substances of a phenolic character are heated with aluminium at the boiling point of the substance in question, there is a rapid action between the metal and the organic compound. If, however, a small amount of water is added to the organic compound, the reaction is prevented, or, if it has already commenced, it is at once inhibited. The reaction

has been studied in the case of (i) a mixture of stearic, palmitic, and oleic acids, (ii) phenol, (iii) cresol (commercial), (iv) a-naphthol, (v) β-naphthol, (vi) methyl alcohol, (vii) ethyl alcohol, (viii) butyl alcohol, (ix) amyl alcohol, and (x) benzyl alcohol. The inhibitory action is explained in the following way. The metal is normally protected by the film which covers it, but this film breaks down when exposed to the attack of the dehydrated substances considered. The presence of even the minutest traces of water is sufficient to inhibit the attack, owing either to the fact that the salts, phenoxides, or alkyloxides, as the case may be, are immediately decomposed by water, aluminium hydroxide being formed, or because the aluminium exposed by the breakdown of the film is immediately reoxidised by water (compare also Gladstone and Tribe, T., 1881, **39**, 9; 1882, **41**, 155).   J. F. S.

The Decomposition of Glycerol in the Presence of Different Catalysts: Formation of Ethyl and Allyl Alcohols. PAUL SABATIER and GEORGES GAUDION (*Compt. rend.*, 1918, **166**, 1033—1039).—The three catalysts used were alumina as a dehydrating catalyst, finely divided copper as a dehydrogenating catalyst, and uranous oxide as a mixed catalyst, capable of producing the two effects. When the vapours or glycerol are passed over alumina at 360°, the products are carbon monoxide, methane, and a trace of carbon dioxide, together with acraldehyde, · which undergoes crotonisation, giving higher aldehydes. Passed over finely divided copper at 330°, the glycerol vapour is decomposed, giving as gaseous products hydrogen and carbon dioxide mixed with some methane and carbon monoxide. The liquid products are ethyl alcohol, allyl alcohol, and some of the higher alcohols. With uranous oxide, more ethyl alcohol and less allyl alcohol are obtained, and more acraldehyde. Further, the proportion of carbon dioxide in the gaseous products is increased. By hydrogenation with nickel at 300°, the products are water and the following gases: hydrogen, methane, ethane, and carbon monoxide and dioxide.   W. G.

The Action of Fumaryl Chloride on Fumaric Acid. G. C. A. VAN DORP and P. J. MONTAGNE (*Rec. trav. chim.*, 1918, **37**, 294—301. Compare *ibid.*, 1906, **25**, 96).—When fumaryl chloride and fumaric acid are heated together at 165° and the products of the reaction separated by means of benzene and treated with aniline, there are obtained maleinanilic acid, fumarodianilide, fumaranilic acid, and fumaric acid. The authors suggest that the condensation of fumaryl chloride and fumaric acid first gives rise to a compound,

$$COCl \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot CO_2H,$$
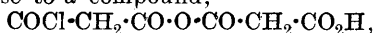
which with another molecule of fumaryl chloride gives the compound $COCl \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot CO \cdot O \cdot CO \cdot CH_2 \cdot COCl$, and this may be decomposed by aniline to give fumarodianilide and fumaranilic acid, whilst the intermediate compound gives either fumarodianilide and fumaric acid or fumaranilic acid.   W. G.

Methyltetronic Acid and its Amide. C. S. HUDSON and L. H. CHERNOFF (*J. Amer. Chem. Soc.*, 1918, **40**, 1005—1007).— Methyltetronolactone was readily prepared by bubbling air through an aqueous solution of rhamnose containing potassium hydroxide. So prepared, it has m. p. 123°, $[a]_D -44.7°$. When dry ammonia was passed through an ethereal solution of the lactone, *methyltetronamide*, m. p. 135° (decomp.), $[a]_D +54.8°$, was obtained.

[EDGAR T. WHERRY.]—Methyltetronolactone has n_a 1·500; n_β 1·515; n_γ 1·535; double refraction strong, 0·035. The axial angle is large, $2E = 120° \pm 10°$. Sign, positive. Methyltetronamide has n_a 1·510; n_β 1·530; n_γ 1·560; double refraction very strong, 0·050.   W. G.

The Isomeric Tetra-acetates of *l*-Arabinose and β-Tri-acetylmethyl *l*-Arabinoside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 992—997. Compare Chavanne, A., 1902, i, 346).—By the acetylation of *l*-arabinose with acetic anhydride and sodium acetate, *α-l-arabinose tetra-acetate*, m. p. 97° (corr.), $[a]_D^{22} +42.5°$, was obtained. This tetra-acetate when heated on a water-bath with acetic anhydride and zinc chloride gave the isomeric *β-l-arabinose tetra-acetate*, m. p. 86°, $[a]_D^{21} +147.2°$. (corr.), Attempts to prepare *α*-triacetylmethyl *l*-arabinoside in a crystalline form from either bromoacetyl *l*-arabinose or *α*-methyl *l*-arabinoside were not successful, but *β-triacetylmethyl* l-*arabinoside*, m. p. 85° (corr.), $[a]_D^{23} +182.0°$, was readily obtained by acetylating β-methyl *l*-arabinoside.   W. G.

Triacetyl-*d*-xylose and *d*-Triacetylmethyl *d*-Xyloside. C. S. HUDSON and J. K. DALE (*J. Amer. Chem. Soc.*, 1918, **40**, 997—1001).—Bromoacetylxylose when shaken with silver carbonate in acetone solution yielded *triacetyl*-d-*xylose*, m. p. 138—141° (corr.), having initial rotation $[a]_D^{21} +70.28°$, which dropped after ten days to 40·8°. This compound, when boiled with acetic anhydride and sodium acetate, yielded *β-tetracetyl-d-*xylose. *α*-Methyl *d*-xyloside on acetylation yielded *α-triacetylmethyl* d-*xyloside*, m. p. 86° (corr.), $[a]_D^{20} +119.55°$. β-Triacetylmethyl *d*-xyloside was similarly prepared.   W. G.

The Glucosazone Reaction. IRA D. GARARD and H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 955—969).—A study of the conditions governing the yield of glucosazone in the osazone test. The authors find that the correct m. p. of phenylglucosazone is 208·0° (corr.), regardless of the method of purification. The maximum yield is obtained when the concentration of phenyl-hydrazine is about 2·0 grams in 20 c.c. The efficiency of the reagent depends on the acidity, and is independent of the negative ion used. The maximum lies close to $P_H^+ = 4.7$, and is best secured with acetic acid and sodium acetate. Within fairly wide limits, the weight of sugar used has very little effect on the per-

centage yield of osazone. Maltose and dextrin retard the formation of glucosazone, and lactose retards it to a still greater extent, whilst starch has very little effect on its formation. The reaction is not complete in less than three hours.   W. G.

The Oxidation of Maltose in Alkaline Solution by Hydrogen Peroxide and by Air. The Preparation and Study of Maltobionic Acid. J. W. E. GLATTFELD and MILTON T. HANKE (*J. Amer. Chem. Soc.*, 1918, **40**, 973—992. Compare Lewis and Buckborough, A., 1914, i, 1199).—The following products of the oxidation of maltose hydrate by hydrogen peroxide in the presence of potassium hydroxide were isolated or detected: formic acid, dextrose, *d*-erythronolactone, *d*-arabonic acid, glycollic, oxalic, and saccharinic acids. By oxidation with a rapid current of air in the presence of the alkali, glyceric acid was also produced.

Maltobionic acid was prepared by the oxidation of maltose by bromine in aqueous solution in the presence of lead carbonate at the ordinary temperature. The acid was isolated as its calcium salt, which had $[\alpha]_D^{20} + 97 \cdot 5°$. The free acid in aqueous solution had $[\alpha]_D^{20} + 98 \cdot 3°$. When hydrolysed with $N/5$-sulphuric acid, it gave gluconic acid and dextrose. It formed a *brucine* salt, m. p. 153°, $[\alpha]_D^{20} + 38 \cdot 05°$.   W. G.

Direct Transformation of Secondary and Tertiary Amines into Nitriles. ALPHONSE MAILHE (*Compt. rend.*, 1918, **166**, 996—997).—The method used to transform di- and tri-*iso*-amylamine into *iso*valeronitrile by passing their vapours over finely divided nickel at 350—380° (compare A., 1917, i, 686) is shown to be generally applicable to secondary and tertiary aliphatic amines. Successful results were obtained with di- and tri-hexyl-amine, di- and tri-amylamine, di- and tri-butylamine, and di- and tri-propylamine.   W. G.

Phosphotungstates of certain Bases and Amino-acids. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, **12**, 5—24).—The phosphotungstates of bases and amino-acids yield figures on analysis which agree with the composition indicated by the formula $R_3,H_3PO_4,12WO_3,xH_2O$, where R is a univalent base. They are readily prepared by the addition of a very slight excess of 30% phosphotungstic acid solution to a solution of the base or its salt in 5% sulphuric acid. The best solvents for recrystallisation are water and 50% alcohol. *Lysine phosphotungstate* crystallises in anhydrous needles; crystalline *phosphotungstates* of *trimethylamine* (octahedra), *isobutylamine* (rhombic prisms), *isoamylamine*, *triisobutylamine, tripropylamine,* and *triisoamylamine* have also been obtained. *Putrescine* and *cadaverine phosphotungstates* closely resemble those of other bases in crystalline form and solubility. They readily dissolve in acetone, but in water they are all practically insoluble. *Phenylethylamine phosphotungstate* crystallises in yellow prisms, p-*hydroxyphenylethylamine phospho-*

tungstate in anhydrous, orange-red octahedra, *β-iminoazolylethyl-amine* and *indole-ethylamine phosphotungstates* in colourless prisms and brownish-purple needles respectively. The *phosphotungstate* of *adenine* crystallises in sulphur-yellow cubical or whetstone-shaped plates, of *hypoxanthine* and of *xanthine* in straw-coloured, cubical plates, and of *uric acid* in reddish-brown cubical plates. These purine phosphotungstates are characterised by very slight solubility, even in acetone. The *phosphotungstates* of *betaine, stachydrine, nicotinic acid, choline, colamine* (*amino-ethyl alcohol*), *urea*, and *guanidine* all crystallise in the form of rhombic prisms.

The study of the solubilities, crystalline forms, and other proper-ties of these phosphotungstates indicates that they are not likely to be of much help in the identification of the parent bases, because of the lack of individual characteristics. The maximum precipita-tion usually occurs when a slight excess of phosphotungstic acid is added, and the final liquid contains 5% of sulphuric acid.

H. W. B.

Preparation and Attempts at Cyclisation of Dedimethyl-piperidine [Dimethylamino-Δ^a-pentene]. AMAND VALEUR and EMILE LUCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 182—185. Com-pare this vol., i, 102, 158).—Dimethylamino-Δ^a-pentene may be prepared by shaking dimethylpiperidinium iodide in aqueous solu-tion with moist silver oxide for three days. After filtering off the silver iodide formed, the alkaline liquid is concentrated under reduced pressure, and finally distilled. Attempts to produce ring formation by heating the base with sulphuric acid, by the action of hypochlorous acid, or by the action of hydriodic acid were not successful.

W. G.

Preparation of some Salts of β-Hydroxytrimethylene-diglycine. HUGO KRAUSE (*Ber.*, 1918, **51**, 542—554. Compare this vol., i, 156).—The following additional salts of β-hydroxytri-methylenediglycine, $OH \cdot CH(CH_2 \cdot NH \cdot CH_2 \cdot CO_2H)_2$, have been prepared: *potassium*, $1H_2O$, and *ammonium* salts, very hygro-scopic; a *barium* salt with $1 \cdot 5H_2O$, by double decomposition of the potassium salt and barium acetate in formalin solution; a comparatively stable *zinc* salt, $C_7H_{12}O_5N_2Zn,EtOH,H_2O$, precipi-tated by adding alcohol to a mixture of formalin and zinc glycine which had been left for ten hours at 50°; another blue *copper* salt, $1H_2O$, which is extremely soluble, but decomposes in solution at below 50°, mainly according to the equation $C_7H_{12}O_5N_2Cu + 2H_2O = Cu(C_3H_6O_3N)_2 + MeOH$, the metallic *salt* ($0 \cdot 5H_2O$) being precipitated as a crystalline, blue powder; mixtures of the mercurous and mercuric salts of the acid corresponding with the last copper salt (hydroxymethylglycine?) were obtained by the action of yellow mercuric oxide on β-hydroxytrimethylenedi-glycine.

Lead gives rise to some characteristic salts. When alcohol is added to a mixture of formalin and a concentrated solution of

s **2**

lead glycine after leaving for ten hours at 50—55°, or to a mixture of the calcium salt and lead nitrate dissolved in formalin, methyl alcohol is expelled and the crystalline *salt*, $Pb(C_3H_6O_3N)_2$, deposited. This becomes oily on kneading with water, and soon changes into the brilliant white *basic* salt, $2PbX_2,Pb(OH)X,H_2O$ ($X = C_3H_6O_3N$). Solid lead glycine and formalin produce a third *salt*, $Pb(O \cdot CO \cdot CH_2 \cdot NH \cdot CH_2)_2O$, which crystallises in glistening, microscopic spangles.   J. C. W.

Dissociation Constants of some Higher Members of the α-Oximino-fatty Acids. CEDRIC STANTON HICKS (T., 1918, **113**, 554—558).—Measurements have been made of the electrical conductivity of solutions of various α-oximino-fatty acids at dilutions varying from 16 to 256. The conductivity increases with time, but comparable values of the ionisation constants were obtained. The progress of the decomposition was investigated in the case of α-oximino*iso*valeric acid by titration with alkali.

The results obtained are discussed in relation to the constitution of the acids, and it is suggested that the oximinic hydroxyl group acts as a negative substituent and not as an alcoholic group, as was implied by Hantzsch and Miolati.   H. M. D.

The Amide Function. J. BOUGAULT (*Compt. rend.*, 1918, **166**, 955—957).—From a comparison of the behaviour and mode of formation of amides with those of acidylsemicarbazinic acids and acidylhydroxamic acids (compare A., 1916, i, 764, 765; 1917, i, 417, 688, 694), the author considers that the constitution of amides is better represented by the formula $R \cdot C \overset{OH}{\underset{NH}{<}}$ (acid type) than by the ordinary formula $R \cdot CO \cdot NH_2$ (basic type). This would explain the existence of metallic derivatives and of Pinner's imino-ethers.   W. G.

The Preparation of Fumaronitrile. The Action of Hydroxylamine on Fumaronitrile. L. McMASTER and F. B. LANGRECK (*J. Amer. Chem. Soc.*, 1918, **40**, 970—973).—The best yield (25%) of fumaronitrile was obtained by heating fumaramide with phosphoric oxide in a current of nitrogen at 170°. With hydroxylamine, the nitrile gave *fumaric acid diamidoxime*, colourless needles, m. p. 212° (decomp.), together with a small amount of a yellow, cotton-like *compound*, m. p. 105° (decomp.), which rapidly darkens in the air.   W. G.

The Stability of Cyclic Systems. J. BÖESEKEN [with (MLLE.) M. DE GROOT and W. VAN LOOKEREN CAMPAGNE (*Rec. trav. chim.*, 1918, **37**, 255—265).—The mixture of *cyclo*hexadienes prepared from 1 : 2-dibromo*cyclo*hexane is, like *cyclo*hexene (compare Böeseken and Sillevis, A., 1914, i, 154), when passed as vapour, mixed with carbon dioxide, over reduced nickel at 180°, converted into benzene and *cyclo*hexane in accordance with the equation $3C_6H_8 = C_6H_{12} + 2C_6H_6$.

An examination of the behaviour of *cyclo*butane-1 : 1-dicarboxylic acid, *cyclo*butanecarboxylic acid and its amide, and *cyclo*butylamine towards hydrogen in the presence of finely divided platinum shows that all these substances resist hydrogenation, the *cyclo*butane ring being, therefore, quite stable under these conditions.

W. G.

Catalytic Reduction of Organic Halogen Compounds. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1918, **51**, 578—585).—The removal of halogen from organic compounds by the action of hydrogen in the presence of a catalyst has been the subject of a number of papers in recent years, and has actually been developed into methods for estimating halogens (see Borsche and Heimbürger, A., 1915, i, 527, 640; Busch and Stöve, A., 1916, ii, 534; Kelber, A., 1917, ii, 215). The authors have also been engaged on this work, and now make a useful summary of their results.

They find that colloidal palladium protected by gum arabic, or palladinised barium sulphate is an efficient catalyst, and that it is usually advisable to have an alkali present to neutralise the halogen hydracid as it is formed. Many substances react even if merely suspended in aqueous alkalis. In the case of halogen derivatives of ethylenic compounds, the halogen may sometimes be removed without saturating the double linking or the halogen derivative of the saturated compound may be formed. Frequently, the reaction proceeds smoothly to hydrogenation and removal of halogen. In the case of dihalogen compounds, it is apparently impossible to obtain mono-derivatives.

As illustrations, the following reductions are described : bromobenzene to benzene; *o*-bromobenzoic acid to benzoic acid; 1 : 4-bromonitrobenzene to aniline; chlorocaffeine to caffeine; chlorocrotonic acid to crotonic acid; *o*-chlorocinnamic acid to β-phenylpropionic acid; dibromosuccinic acid to succinic acid. J. C. W.

***p*-Cymene. I. Nitration. Mononitrocymene.** C. E. ANDREWS (*J. Ind. Eng. Chem.*, 1918, **10**, 453—456).—*p*-Cymene was nitrated by mixing it with an equal weight of sulphuric acid, cooling to 0°, and adding a mixture of nitric and sulphuric acids, the temperature being kept at 0°, or lower. The yield of mononitrocymene was 85%; small quantities of *p*-toluic acid and *p*-tolyl methyl ketone were formed during the nitration. The nitrocymene was reduced to the corresponding amine, which (and also the nitro-compound) consisted of the 1 : 2 : 4-isomeride. [See, further, *J. Soc. Chem. Ind.*, 1918, August.] W. P. S.

Naphthylacetic Acids. II. 3 : 4-Benzphenanthrene. FRITZ MAYER and TRUDI OPPENHEIMER (*Ber.*, 1918, **51**, 510—516).—Weitzenböck and Lieb briefly outlined the most rational method for the synthesis of 3 : 4-benzphenanthrene from β-naphthylacetic acid (A., 1912, i, 548), but this parent substance has since become

more readily available (A., 1916, i, 816), and the synthesis has now been examined in detail.

Sodium β-naphthylacetate, o-nitrobenzaldehyde, and acetic anhydride are heated for some hours at 120—130°, the o-nitro-α-2-naphthylcinnamic acid, m. p. 177—178°, so formed is reduced by ferrous sulphate and ammonia to the o-amino-acid, m. p. 191—192°, which is diazotised and shaken with copper powder, when 3 : 4-benzphenanthrene-1-carboxylic acid, m. p. 218°, is produced. When distilled at 400° in a current of carbon dioxide, this acid gives a poor yield of 3 : 4-benzphenanthrene (I), crystallising in needles or leaflets, m. p. 158—160°, and forming a red *picrate*, m. p. 140—141°.

(I.)   (II.)
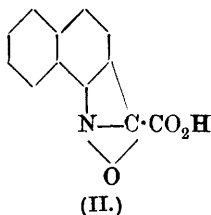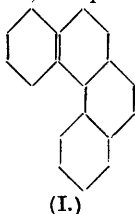
Potassium 1-nitro-2-naphthylacetate loses water when heated with acetic anhydride and zinc chloride, and cannot, therefore, be made to condense with benzaldehyde. The product is *naphthanthroxanic acid* (II), m. p. 218°.

In the above synthesis, there is a possibility of the condensation of the o-amino-α-2-naphthylcinnamic acid leading alternatively to a naphthanthracenecarboxylic acid. Small quantities of by-products are, indeed, formed, but it is difficult to isolate sufficient to ascribe any definite constitution to them.   J. C. W.

Some Halogen Derivatives of Aromatic Amines and their Analysis. I. F. B. DAINS, T. H. VAUGHAN, and W. M. JANNEY (*J. Amer. Chem. Soc.*, 1918, **40**, 930—936. Compare Wheeler, A., 1910, i, 17, 19, 662; 1911, i, 27).—Iodine reacts with chloro- and bromo-anilines to give iodo-derivatives. Thus *p*-bromoaniline gives 4-*bromo-2-iodoaniline*, m. p. 71°, yielding a *hydrochloride*, m. p. 205—206°; an *acetyl* derivative, m. p. 148°; a *benzoyl* derivative, m. p. 152°; 4-*bromo-2-iododiphenylthiocarbamide*, m. p. 167°; 4-*bromo-2-iodophenylallylthiocarbamide*, m. p. 177°; 4-*bromo-2-iodophenylcarbamide*, m. p. 167°; *anisylidene-4-bromo-2-iodoaniline*, m. p. 118°; *cinnamylidene-4-bromo-2-iodoaniline*, m. p. 96°; *piperonylidene-4-bromo-2-iodoaniline*, m. p. 120°; and o-*nitrobenzylidene-4-bromo-2-iodoaniline*, m. p. 159°. If in the above preparation 2 mols. of iodine are used, the product is a mixture of 4-bromo-2-iodoaniline and 4-*bromo-2 : 6-di-iodoaniline*, m. p. 148°.

From *m*-bromoaniline, a 3-*bromoiodoaniline*, m. p. 56°, giving a *hydrochloride*, m. p. 192°, and an *acetyl* derivative, m. p. 199°, is obtained in which the position of the entrant iodine atom has not been definitely ascertained.

p-Chloroaniline yields 4-*chloro*-2(?)-*iodoaniline*, m. p. 46°, giving a *hydrochloride*, m. p. 202°, an *acetyl* derivative, m. p. 150°, and a *benzoyl* derivative, m. p. 145°. 4-*Chlorodi-iodoaniline*, m. p. 129°, giving a *benzoyl* derivative, m. p. 205°, was also prepared.

o-Chloroaniline yielded 2-chloro-4-iodoaniline (compare Werner and Caldwell, T., 1907, **91**, 246). It gave a *hydrochloride*, m. p. 190°, a *benzanilide*, m. p. 165°, and a *phenylcarbamide*, m. p. 175°.

m-Chloroaniline yielded with iodine 3-*chloro*-4-*iodoaniline*, m. p. 65°, giving a *hydrochloride*, m. p. 180°, an *acetyl* derivative, m. p. 170°, and a *benzoyl* derivative, m. p. 144°. The base when diazotised and treated with potassium iodide gave 2-*chloro*-1 : 4-*di-iodobenzene*, m. p. 51°, similar to that obtained in the same way from 2-chloro-4-iodoaniline.

2 : 4-Dichloroaniline only undergoes iodination with difficulty, yielding a small amount of 2 : 4-*dichloro*-6(?)-*iodoaniline*, m. p. 85°, giving a *hydrochloride*, m. p. 180°.

In the majority of the above cases the yields were good, but if the hydrogen of the ring is replaced by two or three methyl groups or by a methoxy-, ethoxy-, or acetylamino-group, the yield of the iodo-derivative was poor, or only resinous products were obtained. The same is true of the methyl- and dimethyl-anilines. Thus ψ-cumidine only gave a small yield of 2-iodo-3 : 4 : 6-trimethylaniline, m. p. 93°. *o*-Anisidine gave 4(?)-*iodo*-2-*methoxyaniline*, m. p. 49°, giving a *hydrochloride*, m. p. 180°, and an *acetyl* derivative, m. p. 176°. *p*-Anisidine only gave a black, waxy, resinous substance, and acetyl-*p*-phenylenediamine behaved in a similar manner.

For the estimation of the halogens in these and similar halogen derivatives, the authors advocate a slight modification of Chablay's method (compare A., 1907, ii, 195), the compound being decomposed by sodium in liquid ammonia. [For details, see *J. Soc. Chem. Ind.*, August.] W. G.

Phenylcarbamates of Terpenic Alcohols and Phenols. F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 266—269).—Phenylcarbamates may be readily obtained in a crystalline state by boiling the alcohol or phenol with the requisite amount of phenylcarbimide in light petroleum (b. p. 170—200°) for a half to one hour. In this way, excellent results were obtained with the three cresols, thymol, menthol, borneol, and eugenol, but good results were not obtained with geraniol or linalool. Camphor may be separated from borneol by this method, the unattacked camphor remaining in solution in the solvent on cooling, whilst the bornyl phenylcarbamate crystallises out. W. G.

Peculiar Action of Methyl Alcohol containing Sulphuric Acid on a β-Arylhydroxylamine. EUG. BAMBERGER (*Ber.*, 1918, **51**, 629—634).—When *m*-2-xylylhydroxylamine is left with a mixture of methyl alcohol and a little concentrated sulphuric acid,

the main product is 5-methoxy-*m*-2-xylidine (A., 1903, i, 624), but this is accompanied by a small quantity of a neutral substance, ammonia being formed as well. The isolation of this compound in a yield of about 4·5% is now described. It is referred to as an "*oxide*," and it crystallises from acetone in glassy prisms, m. p. 139—140°, contains a methoxyl group but no hydroxyl group, and changes into formaldehyde and *m*-2-xylenol when heated at 250—260°. Its formation and constitution are provisionally represented thus:

$$C_6H_3Me_2 \cdot NH \cdot OH + MeOH = OMe \cdot C \underset{\diagdown CMe:CH \diagup}{\overset{\diagup CMe:CH \diagdown}{\longleftarrow O \longrightarrow}} CH + NH_3.$$
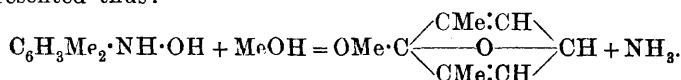
J. C. W.

Acetylation of β-Phenylhydroxylamine. Eug. Bamberger (*Ber.*, 1918, **51**, 636—640).—Phenylhydroxylamine can be readily converted into its N-acetyl derivative by means of acetic anhydride, and the reaction can be adapted to the detection of the base, as follows. A few mg. of the substance are dissolved in cold water, three separate drops of acetic anhydride are added at half-minute intervals, with shaking, followed by a drop of very dilute ferric chloride, when the violet-red colour, changing into grey and then bluish-green, characteristic of the acetyl derivative, develops (see A., 1902, i, 539).

For quantitative purposes, thioacetic acid is a better acetylating agent. The reagents are mixed in dry alcohol, left for a few days, when the solvent is evaporated, the residue rendered alkaline and shaken with ether to remove by-products, and then the solution is acidified and extracted with ether. N-Acetylphenylhydroxylamine (*ibid.*) is soluble in ammonia solution and in 2*N*-sodium carbonate.

Diacetylphenylhydroxylamine, $C_6H_5 \cdot NAc \cdot OAc$, glassy prisms, m. p. 43°, is the product when the base is left with an excess of acetic anhydride.   J. C. W.

The Electrolytic Reduction of *p*-Aminophenol. T. Shoji (*J. Chem. Ind., Tokyo*, 1918, **21**, 117—136).—The principal product of the electrolytic reduction of nitrobenzene in presence of strong sulphuric acid with platinum electrodes is *p*-aminophenol; the use of a carbon cathode is permissible. The concentration of the sulphuric acid electrolyte must not exceed 80%, otherwise there will be a loss of aminophenol by sulphonation. The quantity of sulphuric acid should be five times that of the nitrobenzene; the temperature must be kept at about 80°; a higher temperature induces sulphonation. The current density is 8—9 amperes per sq. dcm., and the *E.M.F.* 6—8 volts. Vigorous agitation of the electrolyte is most important for obtaining a good current efficiency. The cathode chamber must be kept closed to prevent loss of nitrobenzene by volatilisation. Under these conditions, the author obtained 80 grams of crude *p*-aminophenol sulphate from 100

grams of commercial nitrobenzene, yielding 38 grams of free base, or 43% of the theoretical quantity.　　　　　　　　　　J. F. B.

β-Cholestanol, some of its Derivatives and Oxidation Products. GEORGE WILLIAM ELLIS and JOHN ADDYMAN GARDNER (*Biochem. J.*, 1918, **12**, 72—80).—The following derivatives of β-cholestanol have been prepared: *chloroacetate*, $C_{29}H_{49}O_2Cl$, by the action of chloroacetyl chloride in chloroform solution, glistening plates from a mixture of chloroform and ethyl acetate, m. p. 178—179°; *benzoate*, $C_{34}H_{52}O_2$, by the action of benzoyl chloride in pyridine solution, crystallising from ethyl acetate in small plates. It melts at 155° with brilliant fluorescence during the rise of temperature from about 138° to 155°, $[\alpha]_D^{23} + 23 \cdot 3°$ in chloroform solution; *stearate*, $C_{45}H_{82}O_2$, by boiling with stearyl chloride in chloroform solution, flaky crystals from a mixture of alcohol and chloroform, m. p. 100°, $[\alpha]_D^{20} + 18 \cdot 4°$ in ether solution.

On oxidation, β-cholestanol yields β-cholestanone (Diels and Abderhalden, A., 1906, i, 272), which on further oxidation with ammonium persulphate has been found to give a number of lactones of the formula $C_{27}H_{46}O_2$, of which three have been isolated in a more or less pure state and found to melt at 98—100°, 159—161°, and 201—202° respectively. These substances are different, however, from those prepared in a similar manner from coprostanone (Gardner and Goddard, A., 1914, i, 169).　　　　　　H. W. B.

Preparation of Benzoic Acid. WESTON CHEMICAL Co., and J. SAVAGE (Brit. Pat. 116348).—Toluene is converted into benzoyl chloride, with traces of benzylidene chloride, by chlorination at the boiling point; the benzyl chloride is converted into benzyl alcohol by boiling with sodium hydroxide solution or milk of lime, and the alcohol is oxidised to alkali benzoate by means of a hypochlorite in presence of alkali.　　　　　　　　　　A. S.

Catalytic Action of Colloidal Metals of the Platinum Group. XVI. Partial Reduction of Phenylpropiolic Acid with Colloidal Platinum. C. PAAL and ANTON SCHWARZ (*Ber.*, 1918, **51**, 640—643).—It has already been shown that the hydrogenation of phenylpropiolic acid and acetylene can be so controlled under certain conditions, using colloidal palladium as the catalyst, that the corresponding ethylenic compounds are the main products (A., 1909, i, 926; 1915, i, 113). In the case of acetylene, it has also been shown that colloidal platinum is less efficient, and that a mixture of ethylene, ethane, and unreduced acetylene is generally obtained (A., 1915, i, 765). The hydrogenation of phenylpropiolic acid by means of colloidal platinum has now been studied. The yield of malenoid forms of cinnamic acid is found to be much less than when palladium is used, but no β-phenylpropionic acid could be detected under the conditions employed. The deficiency is largely due to the formation of indefinite by-products.　　　　　　　　　　J. C. W.

The Border-line between Isomerism and Polymorphism. III. PAUL PFEIFFER [with J. KLINKERT] (*Ber.*, 1918, **51,** 554—567. Compare A., 1916, i, 24; 1917, i, 140).—It has been shown that certain nitromethoxystilbenes exhibit a kind of isomerism which is termed "cryptoisomerism," and this communication records some further experiments designed to find what conditions are necessary for the display of this phenomenon. It is shown, on the one hand, that the nitro-group may be in the ortho- or para-position in the one benzene nucleus (the question of the meta-position is not discussed), and that, on the other hand, a hydroxyl or methoxyl group, but not alkyl or acyloxy, must be in the para-, but not the ortho-, position in the other benzene nucleus. That is, besides the chromophores, nitro-group and ethylene linking, there must be an auxochrome.

4-Nitro-3-cyanostilbene, obtained by heating *p*-nitro-*m*-toluonitrile with benzaldehyde and a few drops of piperidine at 140°, crystallises in golden-yellow, flat needles, m. p. 187°, and may be hydrolysed by boiling with aqueous-alcoholic potassium hydroxide to *4-nitrostilbene-3-carboxylic acid*, pale yellow, glistening leaflets, m. p. 203°. *4-Nitro-3-cyano-4'-iso*propylstilbene, from cuminaldehyde, forms golden-yellow leaflets, m. p. 132—133°, and *4-nitro-3-cyano-4'-methoxystilbene*, from anisaldehyde, crystallises in brownish-orange, glistening leaflets, m. p. 161°

p-Nitro-*o*-toluonitrile gives rise to *4-nitro-2-cyano-4'-iso*propylstilbene, orange-yellow needles, m. p. 195°, and 4-nitro-2-cyano-4'-hydroxystilbene (*ibid.*, 140). The latter crystallises from glacial acetic acid in orange-yellow needles, m. p. 226°, but if the solution is poured into water, a pure yellow variety is deposited, which becomes permanently orange-yellow on heating at about 200°. It also forms an acetate (*ibid.*) and a *benzoate*, glistening, yellow, flat needles, m. p. 178°.

o-Nitro-*p*-toluonitrile is the parent of the following derivatives: *2-Nitro-4-cyano-4'-iso*propylstilbene, which crystallises with 0·5 mol. AcOH in flat, yellow needles, m. p. 134—138° (142° when deprived of crystal solvent). *2-Nitro-4-cyano-4'-hydroxystilbene*, which exists in two forms, an orange-yellow, giving a pale orange-yellow hydrate, and an orange-red, giving an orange solvate with 1AcOH; the two forms exhibit the same colour in any particular solvent, but the shades vary with the solvent; they both have the same colour at 210° and melt at 230—231°; the acetate has m. p. 225°, not 186° (*ibid.*). *2-Nitro-4-cyano-4'-hydroxy-3'-methoxystilbene*, from vanillin, forms glistening, orange needles, m. p. 207°, and its *acetate*, yellow leaflets, m. p. 170°.

The above 2-nitro-4-cyano-4'-*iso*propylstilbene yields a mixture of chlorides (m. p. 120—125° and 150°) when treated with chlorine in carbon disulphide. When a solution of these in pyridine is exposed to sunlight, 6-*cyano*-4'-iso*propyl*-2-

CO / CN / C·C$_6$H$_4$·CHMe$_2$ / N / O
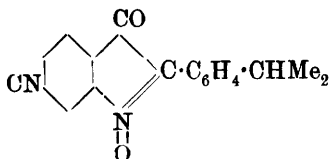
phenylisatogen (annexed formula) is deposited, in orange-red needles, m. p. 220° (compare A., 1916, i, 327). J. C. W.

The Isatoic Acids. J. MARTINET (*Compt. rend.*, 1918, **166,** 952—955).—Three isatoic acids have been obtained by dissolving the corresponding isatins in a known volume of standard potassium hydroxide, and, after the liquid has turned yellow, cooling and adding the calculated quantity of hydrochloric acid. The voluminous precipitate is collected and dried rapidly over phosphoric oxide. In this way, 5-methylisatin yielded *5-methylisatoic acid* (*6-amino*-m-*tolylglyoxylic acid*) (formula I), m. p. 132°; 5:7-dimethylisatin gave *5:7-dimethylisatoic acid* [*2-amino-3:5-dimethylphenylglyoxylic acid*] (formula II), an orange-yellow, crystalline powder, m. p. 215°; α-naphthisatin gave *α-naphthisatoic acid* [*α-aminonaphthyl-β-glyoxylic acid*] (formula III), m. p. 187°.

(I.)   (II.)   (III.)
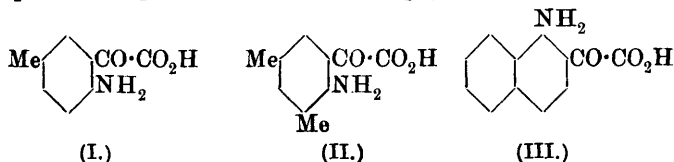
These acids give citron-yellow *potassium* and *barium* salts, orange-yellow *lead* salts, red *copper* salts, and pale yellow *silver* salts.
W. G.

Tetraiodophenolphthalein and Tetrachlorotetraiodophenolphthalein and some of their Derivatives. W. R. ORNDORFF and S. A. MAHOOD (*J. Amer. Chem. Soc.*, 1918, **40,** 937—955).—Tetraiodophenolphthalein was prepared by the method of Classen and Löb (compare A., 1895, i, 539) with slight modifications, and was finally obtained in the form of colourless needles decomposing at 270—272°. Contrary to the opinion of these two authors, the corresponding free carbinolcarboxylic acid could not be obtained, although its potassium and disodium salts were prepared. These salts when heated gave the corresponding salts of tetraiodophenolphthalein. When dry ammonia was passed over the phthalein, a *tetra-ammonia* salt, $C_{20}H_{10}O_4I_4,4NH_3$, was obtained. Tetraiodophenolphthalein gave a *diacetate*, m. p. 246°, a *dibenzoate*, m. p. 298°, and an *oxime*, m. p. 170°.

By the iodination of tetrachlorophenolphthalein in alkaline solution, *tetrachlorotetraiodophenolphthalein*, $\genfrac{}{}{0pt}{}{C_6Cl_4}{CO\cdot O}{>}C(C_6H_2I_2\cdot OH)_2$, decomposing at 240—244°, was obtained, which gave a *diacetate*, m. p. 262°, a *dibenzoate*, m. p. 205°, and with dry ammonia a *tetra-ammonia* salt.

A study of the visible and ultra-violet absorption spectra of these and other phenolphthalein derivatives showed that neutral alcoholic solutions of these phthaleins have absorption spectra of the same type, but that the type changes when the solution becomes alkaline, the characteristic spectrum of the alkaline solutions having

three absorption bands, one at $\lambda = 1600$—1800, the second at $\lambda = 2500$—2700, and the third at $\lambda = 3200$—3600. The magnitude of the first two bands varies greatly with the phthalein. Bromine and iodine in the phenol residues shift all bands towards lower frequencies. Chlorine in the phthalic residue shifts the visible band in the same direction, but the two ultra-violet bands in the opposite direction. The shift increases with the mass of the substituent.   W. G.

Anthranil. XXI. Photochemical Formation of *o*-Nitrosobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, **51**, 606—612).—Sachs and Hilpert (A., 1904, i, 876) exposed a benzene solution of *o*-nitrobenzyl alcohol to the light, in the hope of obtaining *o*-nitrosobenzaldehyde, according to the scheme:

$$C_6H_4{<}^{NO_2}_{CH_2 \cdot OH} \quad \rightarrow \quad C_6H_4{<}^{NO}_{CH(OH)_2} \quad \rightarrow \quad C_6H_4{<}^{NO}_{CHO} + H_2O.$$
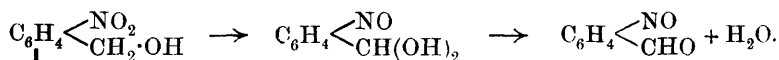
During 1909 and 1910, the author exposed an ethereal solution to the sunlight for about 830 hours at Davos Platz, and now describes the examination of the product. He finds that *o*-nitrosobenzaldehyde is formed, but that it largely suffers oxidation, on the one hand, to *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid, and reduction, on the other hand, to *o*-nitrosobenzyl alcohol, whence anthranil is formed, and probably *oo'*-azoxybenzaldehyde, whence indazolylbenzoic acid and its lactone.   J. C. W.

Anthranil. XXII. *N*-Acetyl-*o*-hydroxylaminobenzaldehyde. EUG. BAMBERGER (*Ber.*, 1918, **51**, 613—629).—The discovery that anthranil is the anhydride of *o*-hydroxylaminobenzaldehyde has naturally led the author to attempt to isolate this compound, but so far it has only been obtained in the form of a very impure, dilute solution (A., 1904, i, 94). The production of the *N*-acetyl derivative is now described, and with this the research is broken off.

"Agnotobenzaldehyde," the primary reduction product of *o*-nitrobenzaldehyde (A., 1907, i, 163), is treated with acetic anhydride, added drop by drop, at 0°, and thus converted into *o*-nitrobenzaldehyde and *N*-*acetyl-o-hydroxylaminobenzaldehyde*, $CHO \cdot C_6H_4 \cdot NAc \cdot OH$, which crystallises from slowly cooling benzene in glassy, triclinic prisms melting at 132° if plunged in a bath at 110° and then heated further, but changing slowly at about 125° into acetylanthranilic acid, $CO_2H \cdot C_6H_4 \cdot NHAc$, thus becoming solid again. The compound dissolves in concentrated sulphuric acid with lemon-yellow colour, anthranil being deposited on dilution. An aqueous suspension gives a deep violet-red colour with ferric chloride. It is soluble in alkali hydroxides or carbonates or aqueous ammonia with lemon- to orange-yellow colour, but the solutions suffer obscure changes when kept. The *phenylhydrazone* forms golden-yellow, silky needles, m. p. 120—120·5° (180—181° on one occasion), and dissolves in sodium hydroxide with magenta

colour. When a solution of bleaching powder is slowly added to a cold, supersaturated solution of the aldehyde in water, o-nitrosobenzaldehyde is precipitated, the yield being as high as 85%. o-Nitrobenzaldehyde is also formed if too much hypochlorite is used, whilst the addition of perhydrol to a solution in glacial acetic acid causes the precipitation of a " *peroxide* " (?),

$$CHO \cdot C_6H_4 \cdot NAc \cdot O \cdot OH,$$
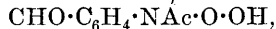
in satiny, flat needles, m. p. 110·5—111°, which gives the peroxide reaction with titanium dioxide in sulphuric acid.   J. C. W.

Bornylenecamphor and a New Dicamphor, *iso*Dicamphor.

MARCEL GUERBET (*Compt. rend.*, 1918, **166**, 1049—1052).—When camphor is heated with sodium methoxide in methyl-alcoholic solution, the main product is not bornylenecamphor, only a trace of this compound being obtained, but iso*dicamphor*,

$$C_8H_{14} {<}_{CO}^{CH-CH} {}_{CO-}^{} {>} C_8H_{14},$$
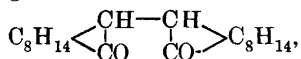
m. p. 196°, $[\alpha]_D^{18} + 64°54'$ (in alcohol).

At 250° it is slowly converted into camphor. It yields a *monoxime*, m. p. 159—160°, and a *dioxime*, m. p. 235°. On bromination, it gives *bromo*iso*dicamphor*, $C_{20}H_{29}O_2Br$, m. p. 161°, and *dibromo*iso*dicamphor*, m. p. 132°. When oxidised by dilute nitric acid, it yields camphoric acid.   W. G.

Nomenclature of Hydrocyanic Glucosides of the Amygdalin Group.

EM. BOURQUELOT (*J. Pharm. Chim.*, 1918, [vii], **17**, 359—361).—When hydrolysed with hot concentrated hydrochloric acid, prunasin yields *l*-phenylglycollic acid, prulaurasin gives inactive phenylglycollic acid, and sambunigrin (A., 1905, i, 912) *d*-phenylglycollic acid. Under the same conditions, amygdalin gives the *l*-acid, *iso*amygdalin· the inactive acid, and *d*-amygdalin the *d*-acid. The relations of these glucosides is therefore as follows :

Monoglucosides, $C_{14}H_{17}O_6N$	Diglucosides, $C_{20}H_{17}O_{11}N$.
Prunasin	*l*-Amygdalin or gluco-prunasin
Prulaurasin	*iso*Amygdalin or gluco-prulaurasin.
Sambunigrin	*d*-Amygdalin or gluco-sambunigrin.

The diglucosides may be converted into the corresponding monoglucosides by the action of dry bottom-fermentation yeast.
      W. P. S.

A New Group of *cyclo*Propane Derivatives. I. Action of Phenylacyl Haloids on 3-Acylcoumarins in the Presence of Sodium Alkyloxides.

OSKAR WIDMAN (*Ber.*, 1918, **51**, 533—541). —When 3-acetylcoumarin and ω-halogenoacetophenones are mixed in cold alcohol and treated with one atomic proportion of sodium ethoxide solution, two products are obtained which are indifferent towards permanganate, the ethylene linking in the coumarin ring being saturated by the addition of the phenacylidene residue,

*cyclo*propane derivatives resulting. The chief product is 3-*acetyl-3 : 4-phenacylidenecoumarin*, $\begin{array}{c}C_6H_4-CH-\\|\quad\quad|\\O\cdot CO\cdot CAc\end{array}\!\!>\!\!CHBz$, which crystallises in silky needles, m. p. 184°, and the other compound, which is the more soluble in alcohol, is *ethyl α-acetyl-αβ-phenacylidenecoumarate* [*ethyl 1-acetyl-2-benzoyl-3-o-hydroxyphenylcyclopropane-1-carboxylate*], $CHBz\!\!<\!\!\begin{array}{c}CAc\cdot CO_2Et\\|\\CH\cdot C_6H_4\cdot OH\end{array}$. This crystallises in brilliant, quadratic prisms, m. p. 117°, and forms an *acetate*, lustrous octahedra, m. p. 89°. The condensation must proceed most readily, for the ω-halogenoacetophenones give rise to the 2-halogeno-3 : 4-oxido-3 : 5-diphenyltetrahydrofurans when left with sodium alkyloxides alone (A., 1913, i, 1219), and no trace of these compounds is found in the present instance.

Similar compounds are produced by other 3-acylcoumarins. Thus 3-*propionylcoumarin*, very long, silky needles, m. p. 134° (from salicylaldehyde and ethyl propionylacetate) gives rise to 3-*propionyl-3 : 4-phenacylidenecoumarin*, needles, m. p. 157—158°, and *ethyl α-propionyl-αβ-phenacylidenecoumarate*, prisms or irregular hexagonal tablets, m. p. 109—110°. 3-Benzoylcoumarin, m. p. 135—136° (compare Knoevenagel and Arnot, A., 1905, i, 65), forms 3-*benzoyl-3 : 4-phenacylidenecoumarin*, tablets, m. p. 189—190°, there being also a suggestion of *cis-trans*-isomerism in this case. Ethyl coumarin-3-carboxylate forms *ethyl 3 : 4-phenacylidenecoumarin-3-carboxylate*, flat needles, m. p. 176—177°; *methyl coumarin-3-carboxylate*, m. p. 116—117° (from methyl malonate and salicylaldehyde), yields the corresponding *methyl* ester, m. p. 183°, mixed with "*methyl ethyl αβ-phenacylidenesalicylidenemalonate*" [*methyl ethyl 2-benzoyl-3-o-hydroxyphenylcyclopropane-1 : 1-dicarboxylate*], $\begin{array}{c}CO_2Me\\CO_2Et\end{array}\!\!>\!\!C\!\!<\!\!\begin{array}{c}CHBz\\|\\CH\cdot C_6H_4\cdot OH\end{array}$,$H_2O$, this being the more soluble in alcohol, and crystallising in glistening rhombohedra, m. p. 96°. The 3 : 4-phenacylidenecoumarin-3-carboxylates are hydrolysed by 4% sodium hydroxide to salicylaldehyde, phenacylmalonic acid, $CH_2Bz\cdot CH(CO_2H)_2$, and *α-hydroxy-γ-benzoyl-α-o-hydroxyphenylpropane-ββ-dicarboxylic acid*,

$$OH\cdot C_6H_4\cdot CH(OH)\cdot C(CO_2H)_2\cdot CH_2Bz,$$

short prisms, m. p. 126—128° (decomp.). 3-Cyanocoumarin also condenses with ω-bromoacetophenone, yielding 3-*cyano-3 : 4-phenacylidenecoumarin*, in slender needles, m. p. 218°.   J. C. W.

*epi***Berberine.** WILLIAM HENRY PERKIN, jun. (T., 1918, **113**, 492—522).—An attempt to prepare *epi*berberinium hydroxide and to compare its properties and those of its salts with those of berberinium hydroxide and its salts (compare T., 1916, **109**, 833). Attempts to demethylate cryptopine by the method of Diels and Fischer as applied to codeine (compare A., 1914, i, 989) were not successful. It was noticed, however, that many methochlorides, such as 6 : 7-dimethoxy-2-methyltetrahydro*iso*quinoline, decompose

at their melting points, giving off methyl chloride. β-Tetrahydro-anhydroberberine methochloride (Pyman, T., 1913, **103**, 828) in this way loses its methyl chloride. *iso*Cryptopine chloride when heated in small quantities under diminished pressure decomposes at 260°, giving methyl chloride and *dihydroanhydroepiberberine* (annexed formula), crystallising in iridescent, golden, monoclinic plates [$a:b:c = 1·163:1:0·995$; $\beta = 97°15'$], m. p. 172—174°. It gives a *hydrochloride*, $C_{20}H_{19}O_4N,HCl,3H_2O$, a *hydrobromide*, a *methosulphate*, m. p. 260° (decomp.), and a *methiodide*, m. p. 245° (decomp.). The methosulphate when boiled with methyl-alcoholic potassium hydroxide yields anhydrocryptopine (T., 1916, **109**, 975). *Tetrahydroanhydroepiberberine*, $C_{20}H_{21}O_4N$, m. p. 170—171°, is obtained either by the action of heat on *iso*dihydrocryptopine α-chloride or β-chloride, or by the reduction of dihydroanhydro*epi*berberine with zinc or tin and hydrochloric acid. It is a strong base, and gives a *hydrochloride*, a *sulphate*, a *nitrate*, and a *methosulphate*, m. p. 255—260° (decomp.), which is decomposed by boiling with methyl-alcoholic potassium hydroxide, giving anhydrodihydrocryptopine.
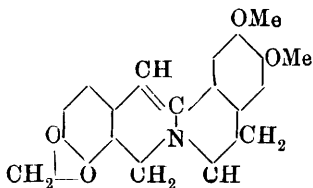
When dihydroanhydro*epi*berberine or the tetrahydro-derivative is acted on by oxidising agents, such as bromine, iodine, or dilute nitric acid, or preferably by mercuric acetate in acetic acid solution, various, deep orange salts of *epi*berberine are obtained by suitable subsequent treatment. In this way, the author has prepared epi*berberinium chloride*, $C_{20}H_{18}O_4NCl,4H_2O$, which gives a *platinichloride*, the *sulphate*, the *iodide*, and the *picrate*, m. p. 222°.

*epi*Berberinium sulphate is decomposed by aqueous sodium hydroxide in the same manner a's is berberinium sulphate, and yields *oxy*epi*berberine*, $C_{20}H_{17}O_5N$, m. p. 240—241°, and dihydroanhydro-*epi*berberine. Oxy*epi*berberine gives an *acetate*,

$$C_{20}H_{17}O_5N,C_2H_4O_2,$$
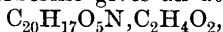
which is dissociated by water or heat. By the action of hydrochloric acid, oxy*epi*berberine is converted into iso*oxy*epi*berberine*, needles. Although it was not found possible to isolate *epi*berberine itself, its O-methyl and O-ethyl derivatives have been obtained in a pure condition by the action of sodium methoxide and ethoxide respectively on *epi*berberinium chloride. O-*Methyl*epi*berberine* separates in golden prisms, m. p. 150—152° (decomp.), and O-*ethyl*epi*berberine*, $C_{20}H_{18}O_4(OEt)N$, in needles, m. p. 135—136° (decomp.). Both these compounds dissolve readily in boiling acetone, and from the solution, on cooling, anhydro*epi*berberineacetone, $C_{20}H_{17}O_4N,C_3H_6O$, m. p. 162°, separates. The author discusses fully the nomenclature of berberine and its salts. For experimental details, see the original, **W. G.**

Metallic Derivatives of Alkaloids. JITENDRA NATH RAKSHIT (T., 1918, **113**, 466—471).—Sodium and potassium derivatives of codeine and narcotine and the sodium derivative of cotarnine were obtained by boiling the alkaloids with the respective metals in benzene. *Sodium codeine*, $C_{18}H_{20}O_3NNa$, is a brownish-yellow powder which, in aqueous solution, does not give any precipitate with Mayer's reagent until the mixture is acidified. *Potassium codeine*, $C_{18}H_{20}O_3NK$, forms reddish-brown crystals. *Sodium narcotine*, $C_{22}H_{22}O_7NNa$, was obtained as a reddish-yellow powder, which is decomposed in aqueous solution by carbon dioxide, narcotine being liberated. *Dipotassium narcotine*, $C_{22}H_{21}O_7NK_2$, is a bright yellow, crystalline powder. *Tetrasodium cotarnine*, $C_{12}H_{11}O_4NNa_4$, is a hygroscopic, bright yellow, crystalline powder. *Calcium morphinate*, $(C_{17}H_{18}O_3N)_2Ca$, was obtained by triturating morphine with calcium hydroxide in the presence of alcohol as a brown, non-deliquescent powder, which is readily decomposed by carbon dioxide.   W. G.

The Presence of a Fixed Alkaloid in the Common Broom. AMAND VALEUR (*Compt. rend.*, 1918, **167**, 26—28).—From the mother liquors resulting from the crystallisation of sparteine sulphate as prepared from *Sarothamnus scoparius*, the author has isolated another alkaloid, *sarothamnine*, which readily forms crystalline compounds with various solvents. Thus *sarothamnine-chloroform*, $C_{15}H_{24}N_2,\tfrac{1}{2}CHCl_3$, has m. p. 127° and $[\alpha]_D -38\cdot7°$; *sarothamnine-ethyl alcohol*, $C_{15}H_{24}N_2,\tfrac{1}{2}EtOH$, has m. p. 90°, $[\alpha]_D -25\cdot6°$. It unites similarly with methyl alcohol and benzene. The alkaloid is unsaturated, since it reduces aqueous potassium permanganate in the cold.   W. G.

Pyridine Derivatives from $\alpha\beta$**-Dichloroethyl Ether and Ethyl** β**-Aminocrotonate, and related Amino-compounds. II.** ERICH BENARY (*Ber.*, 1918, **51**, 567—577. Compare A., 1911, i, 320).—The action of various agents on the 4-chloromethylpyridine derivatives described in the earlier paper, and the production of similar esters from acetylacetonamine and benzoylacetonamine are dealt with in this paper.

The reaction between $\alpha\beta$-dichloroethyl ether and ethyl β-amino-crotonate, whereby ethyl 2 : 6-dimethyl-4-chloromethyl-1 : 4-di-hydropyridine-3 : 5-dicarboxylate is formed, is best effected in the presence of dilute aqueous ammonia. The ester reacts with potassium hydrosulphide to form the 4-*thiolmethyl* derivative, which crystallises in slender needles, m. p. 86—87°, and with bromine to give a *dibromo-dibromide*, pale yellow needles, m. p. 109—110°, which may be oxidised by pure nitric acid to the corresponding *ethyl dibromo-2 : 6-dimethyl-4-chloromethylpyridine-3 : 5-dicarboxylate dibromide*, $C_{14}H_{16}O_4NClBr_4$, m. p. 114—115°.

More important results may be obtained with ethyl 2 : 6-dimethyl-4-chloro(or iodo-)methylpyridine-3 : 5-dicarboxylate. Hydrolysis with boiling 10% sodium hydroxide gives rise to the *lactone* of

2 : 6-*dimethyl*-4-*hydroxymethylpyridine*-3 : 5-*dicarboxylic acid*, hard crystals, m. p. 213°. With alcoholic ammonia at 100—110°, the product is the *lactam* of *ethyl hydrogen* 2 : 6-*dimethyl*-4-*amino-methylpyridine*-3 : 5-*dicarboxylate*, needles, m. p. 168—169°, which may be hydrolysed by boiling alcoholic potassium hydroxide to the free *lactamic acid*, $\begin{matrix} \text{CMe·C(CO}_2\text{H):C·CH}_2 \\ \text{N·CMe} = = = \text{C—CO} \end{matrix}$ >NH, pale yellow, microscopic needles, decomp. 300°. Potassium hydrosulphide forms the *thiolactone* of *ethyl hydrogen* 2 : 6-*dimethyl*-4-*thiolmethylpyridine*-3 : 5-*dicarboxylate*, in long, silky, pale pink needles, m. p. 115—116°, and this may be hydrolysed to the free *thiolactonic acid*, decomp. 272°. Potassium cyanide produces *ethyl* 2 : 6-*dimethyl*-4-*cyano-methylpyridine*-3 : 5-*dicarboxylate*, in colourless needles, m. p. 66—67°.

Acetylacetonamine and *αβ*-dichloroethyl ether react in the presence of dilute aqueous ammonia to form 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*chloromethyl*-1 : 4-*dihydropyridine*, pale yellow, hard needles, m. p. 151°, which may be oxidised by nitric acid to 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*chloromethylpyridine*, colourless needles, m. p. 76—77°. This reacts with sodium iodide to form the corresponding *iodo*-derivative, m. p. 116—118°, and with alcoholic ammonia at 50—60° to give the "*anhydride*" of 3 : 5-*diacetyl*-2 : 6-*dimethyl*-4-*aminomethylpyridine*, $\begin{matrix} \text{CMe·CAc:C–CH}_2 \\ \text{N·CMe} = = \text{C·CMe} \end{matrix}$ >N, which crystallises in dark reddish-brown needles, decomp. above 136°.

Benzoylacetonamine yields 3 : 5-*dibenzoyl*-2 : 6-*dimethyl*-4-*chloro-methyl*-1 : 4-*dihydropyridine*, in sulphur-yellow needles, m. p. 183°, which forms a *nitro*-derivative, m. p. 168—169°, instead of suffering oxidation, when treated with nitric acid. J. C. W.

The Isatins which contain a Quinoleic Nucleus. J. MARTINET (*Compt. rend.*, 1918, **166**, 998—1000).—Tetrahydro-quinoline is converted by the action of ethyl mesoxalate into ethyl 1 : 7-trimethylenedioxindole-3-carboxylate, m. p. 174° (compare A., 1913, i, 756). In the same way, the author has prepared *ethyl 5-methyl*-1 : 7-*trimethylenedioxindole*-3-*carboxylate*, m. p. 162°, and *ethyl 5-methyl*-1 : 7-*α-methyltrimethylenedioxindole*-3-*carboxylate* (annexed formula), m. p. 108°. These esters when hydrolysed by alkalis and the product acidified give the corresponding isatins, which yield salts of the intermediate, unstable isatoic acids. Thus 1 : 7-*trimethyleneisatin*, red needles, m. p. 195°, giving a *phenyl-hydrazone*, m. p. 150°, yields the *potassium*, *copper*, and *lead* salts of 1 : 7-trimethyleneisatoic acid; 5-*methyl*-1 : 7-*trimethyleneisatin*, m. p. 185°, gives a *phenylhydrazone*, m. p. ·177°, and yields *potassium* and *copper* 5-*methyl*-1 : 7-*trimethylene-isatoates* 5-*methyl*-1 : 7-*α-methyltrimethyleneisatin*, m. p. 165°,
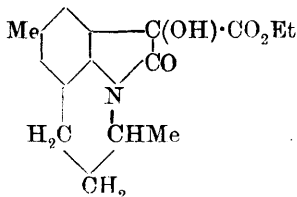
gives a *phenylhydrazone*, m. p. 141°, and the *barium* salt of the corresponding isatoic acid. The isatins when treated with hydrocyanic acid and the cyano-compound hydrolysed with hydrogen chloride in alcoholic solution are reconverted into the dioxindole-3-carboxylic esters.   W. G.

Yellowish-brown Vat Dyes. SYNTHETIC PATENTS CO., NEW YORK (U.S. Pat. 1266092).—The new vat-dyes are compounds of the type

$$NR_2 \overset{\diagup\diagdown}{\underset{\diagdown\diagup}{\left[\,\text{II}\,\right]}} \overset{-CO\cdot C\,:\,C————}{\underset{——NH\ CO\cdot NH\cdot}{}} \left[\,\text{I}\,\right] \overset{\diagup\diagdown}{\diagdown\diagup}$$
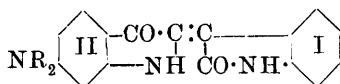
in which the benzene nucleus, I, contains halogen, the nucleus, II, may contain halogen, and R may be oxygen or hydrogen. As an example, the *compound* produced by the interaction of 5:7-dichloro-isatin and 6-aminoindoxyl is cited; this is a dark brown, lustrous, crystalline powder,· soluble in concentrated sulphuric acid with reddish-violet colour, which dyes cotton from the alkaline hyposulphite vat in yellowish-brown shades, fast to washing, light, and chlorine.   J. C. W.

Alloxan and Alloxantin. EINAR BIILMANN and JOHANNE BENTZON (*Ber.*, 1918, **51**, 522—532).—Thunberg has recently shown that the solubility of alloxantin in water is greatly depressed by the addition of alloxan, and suggests, therefore, that alloxantin is the alloxan salt of dialuric acid (A., 1916, i, 635). Some careful determinations of these solubilities have now been made, and the results show that the solubility of alloxantin in the presence of alloxan obeys the mass law, and that it is possible to calculate the dissociation constant for alloxantin.

According to Richter's oxonium formula (A., 1911, i, 757), which is favoured by Thunberg, the dissociated particles would be an alloxan cation and a dialuric anion. Alloxan might be expected, therefore, to give the same cation in contact with hydrochloric acid, and consequently raise the freezing point of the acid, but in reality it has no such influence. Furthermore, solutions of alloxan become distinctly yellow on heating, but colourless again on cooling, owing to the formation and hydrolysis of the anhydride (Biltz, A., 1913, i, 166). This shows that alloxan is very susceptible to hydroxyl compounds, and excludes a quinonoid configuration for both alloxan and alloxantin. In fact, the arguments advanced are in favour of the formula

$$CO\underset{NH\cdot CO}{\overset{NH\cdot CO}{<}}\hspace{-2pt}>C(OH)\cdot O\cdot CH\underset{CO\cdot NH}{\overset{CO\cdot NH}{<}}\hspace{-2pt}>CO,$$
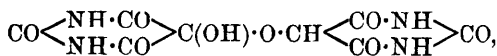
for alloxantin. This "alcoholate" formula was first proposed by Slimmer and Stieglitz (A., 1904, i, 634).

The solubility determinations were carried out in an atmosphere

of carbon dioxide or nitrogen, the apparatus being described. Alloxantin was determined by titration with a solution of iodine in potassium iodide, and alloxan + alloxantin found from the result of a Kjeldahl estimation. The solubility of alloxantin, $C_8H_6O_8N_4,2H_2O$, in water at 25° is 0·2885 gram per 100 c.c. (or grams), of which about 22% is undissociated. The mean value of K at 25°= 38·7. J. C. W.

The Action of Hydrazine Hydrate on Cyanotetrazole. I. LIFSCHITZ and W. F. DONATH (*Rec. trav. chim.*, 1918, **37**, 270—293).—A more detailed account of work already published (compare A., 1915, i, 465; 1916, i, 436), and an elaboration of the work of Curtius, Darapsky, and Müller (compare A., 1916, i, 84) in reply to these authors.

When the mixture obtained by passing cyanogen into aqueous azoimide is treated with hydrazine hydrate, in addition to the bishydrazonium salt of bistetrazole, there is obtained the *hydrazonium* salt of *tetrazolecarbohydrazidine*,

$$N_2H_4 \cdot CN_4H \cdot C\!\!<^{NH_2}_{N \cdot NH_2}$$
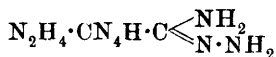
or $N_2H_4 \cdot CN_4H \cdot C\!\!<^{NH}_{NH \cdot NH_2}$, m. p. 276°, which gives a *silver* salt, and when treated with nitrous acid yields bistetrazole. The hydrazonium salt when treated with aldehydes gives condensation products having the general composition $CHR{:}C_2H_3N_7$. Thus benzaldehyde gives a *compound*, m. p. 248°; anisaldehyde a *compound*, m. p. 252°; and *p*-nitrobenzaldehyde a *compound*, m. p. 240°.

The authors describe an *ethyl* derivative of ditetrazyldihydrotetrazine and an *ethyl* derivative of ditetrazyltetrazine. W. G.

Diazotisation of Nitrosobenzene. EUG. BAMBERGER (*Ber.*, 1918, **51**, 634—636).—Nitrosobenzene may be almost completely converted into a benzenediazonium salt by adding a very concentrated solution of sodium nitrite to a solution in cold acetic acid, or by means of amyl nitrite. The question is raised, which is the active agent, nitrous acid, nitrogen peroxide, or nitric oxide? No answer is given in the case of nitrous acid, but it has now been proved that dry nitrogen peroxide has no diazotising action, its only effect being that of an oxidising agent. Nitric oxide was shown some twenty years ago to convert nitrosobenzene into benzenediazonium nitrate. J. C. W.

Action of Di-*p*-diazo-*m*-tolylmethane Chloride on Naphthol- and Naphthylamine-sulphonic Acids. I. JAMES H. STEBBINS. jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 445—448).—When *o*-toluidine is dissolved in dilute hydrochloric acid, mixed with formaldehyde, and kept at 70—76° for four hours, *di-p-aminodi-*m*-tolylmethane*, $C_6H_2(C_6H_3Me \cdot NH_2)_2$, is obtained; it crystallises in rhombic prisms, m. p. 149°. When this is diazotised, it yields *di-p-diazo-*m*-tolyl-*

methane chloride, $CH_2(C_6H_3Me \cdot N_2Cl)_2$. On mixing the diazotised solution with sodium *α*-naphthol-4-sulphonate, a copious, blood-red precipitate is obtained which seems to have the composition $\overset{4}{N_2}Cl \cdot \overset{3}{C_6}\overset{1}{H_3}Me \cdot CH_2 \cdot \overset{3}{C_6}\overset{4}{H_3}\overset{7}{Me} \cdot N_2 \cdot \overset{1}{C_{10}}\overset{4}{H_5}(OH) \cdot SO_3H$, and is gradually transformed into

$$OH \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_3Me \cdot N_2 \cdot C_{10}H_5(OH) \cdot SO_3H.$$

The *sodium* and *barium* salts of the latter acid were prepared. In the presence of alcohol, two molecules of the naphtholsulphonic acid combine with the diazo-compound, and a heavy, carmine precipitate of the sodium salt of the acid,

$$CH_2[C_6H_3Me \cdot N_2 \cdot C_{10}H_5(OH) \cdot SO_3H]_2,$$
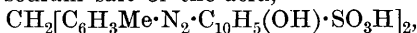
is formed. The diazotised solution when mixed with an aqueous sodium carbonate solution of *β*-naphthol-3 : 6-disulphonic acid, yields a scarlet-red precipitate of the salt,

$$CH_2[C_6H_3Me \cdot N_2 \cdot C_{10}H_4(SO_3Na)_2 \cdot OH]_2.$$
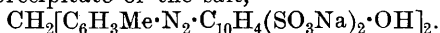
W. P. S.

Nucleic Acid and its Analytical Examination. A. CHASTON CHAPMAN (*Analyst*, 1918, **43**, 259—263).—The chief difficulties in the preparation of pure nucleic acid are the complete removal of proteins and the prevention of the acid becoming contaminated with its own products of decomposition. Hydrolysis must therefore be effected under definite conditions. It is uncertain whether all nucleic acids are identical with one or other of the two typical nucleic acids obtained from yeast and from the thymus gland, but in practice yeast-nucleic acid is frequently described as "plant nucleic acid." Its chief products of hydrolysis are: guanine, adenine, cytosine, uracil, *d*-ribose (pentose), and phosphoric acid. Nucleic acid of animal origin, when hydrolysed, yields: guanine, adenine, cytosine, thymine, lævulic acid (from a hexose), and phosphoric acid. Plant nucleic acid is a white, friable, odourless substance with the formula $C_{38}H_{50}O_{29}N_{15}P_4$. It is nearly insoluble in water, but is readily soluble in solutions of alkali acetates, from which hydrochloric acid precipitates it as a curd-like precipitate soluble in excess of the acid. It forms characteristic salts with copper, calcium, and silver, and a strong aqueous solution of sodium nucleate gelatinises. It may also be identified by yielding guanine and adenine as distinctive products of hydrolysis. [See, further, *J. Soc. Chem. Ind.*, 1918, 441A.] C. A. M.

The Nature of the Aqueous Medium in the Enzymic Hydrolysis of Oils. Y. TANAKA (*J. Chem. Ind., Tokyo*, 1918, **21**, 112—117).—Referring to the experiments by Kita (A., 1918, i, 274), the author suggests that he was working with a lipase preparation still containing zymogen not completely activated by the previous treatment with acid, and consequently subject to a further stimulation when allowed to act on fats in an acidified medium. Further experiments have been made according to the author's method, by triturating pressed castor beans with eight

times their weight of $N/10$-acetic acid, washing, and drying the insoluble residue. A series of hydrolyses was carried out with 2 grams of the activated lipase powder and 25 grams each of soja bean oil at 38—39°, in 10 c.c. of aqueous substratum, containing increasing amounts of $N/10$-sulphuric acid. The percentage of oil hydrolysed in one hour decreased with increasing acidity of the medium, thus: with 0·0 c.c. acid, 58·4%; 0·5 c.c., 53·8%; 1·0 c.c., 51·2%; 2·0 c.c., 40·0%. The results after five hours were in the same order. Thus it is confirmed that castor bean lipase which has been treated with the optimum quantity of acid and washed acts most energetically in neutral media. J. F. B.

Action of Ethyl Alcohol and Acetone on Lipase. GEN-ITSU KITA and MINORU OSUMI (*J. Tokyo Chem. Soc.*, 1918, **39**, 13—22). —Connstein, Hoyer, and Wartenburg (A., 1903, i, 218), Hoyer (A., 1907, ii, 192), and Falk (A., 1913, i, 664) have already observed that the activity of lipase is destroyed by ethyl alcohol. The author has repeated this investigation, and finds that when the activity of lipase has been destroyed by alcohol, it cannot be restored by any treatment. Contrary to the statements of Hoyer and Falk, acetone has no particular influence on the activity.
S. H.

Physiological Chemistry.

Transport of Carbon Dioxide by Solutions of Sodium Hydrogen Carbonate. G. A. Buckmaster (*Proc. physiol. Soc.*, 1918, xvi—xvii; *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 177).—The dissociation tensions of solutions of varying quantities of pure sodium hydrogen carbonate in boiled-out water were determined at 38° in an atmosphere of air, nitrogen, and a mixture of nitrogen and carbon dioxide respectively. The average dissociation tension was 2·25 mm. of mercury in air and carbon dioxide respectively. In a mixture of nitrogen and carbon dioxide, with tensions of the latter within the range of alveolar air, there was no dissociation and carbon dioxide was actually absorbed, and it is therefore improbable that the transport of carbon dioxide in the blood is a function of the sodium carbonate.   S. B. S.

Viscosity of Blood. J. W. Trevan (*Biochem. J.*, 1918, **12**, 60—71).—The viscosimeter is blown from glass tubing of 0·8 mm. diameter for the large size, using 2 c.c. of blood, and 0·2 mm. diameter for the small form requiring only 1 c.c. of blood. In the large model, the bulb, *C* (see Fig.), holds rather less than 1 c.c.; the other dimensions are in proportion. The funnel, *D*, is made from a test-tube (1·25 cm.) drawn out and fused on, and holds about

5 c.c. The blood is mixed with a little hirudin in D and allowed to run into C. The instrument is then placed in a thermostat at 40° for ten minutes. The bulb, C, is then emptied into D by slowly blowing down the rubber tube, E, until the whole of the blood is in D. The corpuscles are mixed with the plasma by stirring with a coiled wire, and then the blood is allowed to flow back again into C, the time of flow from B to A being noted with a stop-watch, and the blood in D being stirred continually with the coiled wire.
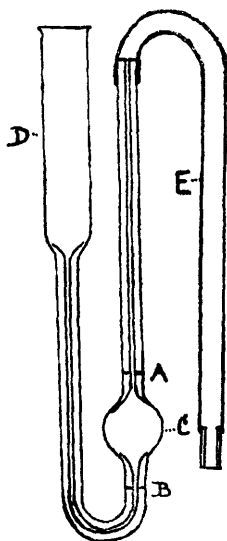
The results show that the viscosity of the blood is directly proportional to that of the plasma over a very wide range of plasma viscosity provided the volume of corpuscles remains constant. Any increase in the number of corpuscles greatly increases the viscosity of the blood. The relation is expressed by the formula $100/P = (n/n-1)^3$, where P is the percentage volume of corpuscles in the blood and n is the ratio of the viscosity of the whole blood to that of the plasma. The bearing of the results on the interpretation of certain phenomena associated with inflammation, infarction, and blood circulation generally are discussed.

H. W. B.

Physiology of Blood-sugar. II. Lépine's "Sucre virtuel." RICHARD EGE (*Biochem. Zeitsch.*, 1918, **87**, 92—103).—According to Lépine (numerous papers, 1902—1914), part of the sugar in blood is free ("sucre immedial"), whereas part is bound in chemical combination and only set free after hydrolysis ("sucre virtuel"). Using ferments and other treatment, the author has been unable to confirm Lépine's statement as to the existence of the two forms of blood-sugar.   S. B. S.

Influence of Morphine, and of Morphine with Ether Anæsthesia, on the Dextrose in the Blood. ELLISON L. ROSS (*J. Biol. Chem.*, 1918, **34**, 335—342).—The subcutaneous injection of morphine into a dog is followed by a pronounced glycosuria, which, although not so intense as that which may be produced by simple ether anæsthesia, is nevertheless increased by subsequent administration of ether, so that the final degree of hyperglycæmia reached is approximately the same, either with or without the preliminary morphine injection.   H. W. B.

Rate of Dialysis of the Dextrose in the Blood in Experimental Diabetes. ISRAEL S. KLEINER (*J. Biol. Chem.*, 1918, **34**, 471—487).—The rate of dialysis of dextrose from blood into Ringer's solution is dependent on the state of the animal from which the blood is obtained. The dextrose in the blood from a

diabetic animal dialyses at an irregular rate showing more or less completely arrested dialysis, usually about two hours after the commencement of the experiment. The dialysis of the dextrose in normal blood, to which dextrose has been added to bring it to the same dextrose content as the diabetic blood, occurs at a uniform rate. The author suggests that in diabetes the dextrose exists partly in a combined state in the blood, which tends to hinder its dialysis (compare Michaelis and Rona, A., 1909, ii, 68).

H. W. B.

Acetone Substances in the Blood in Diabetes. ERNEST LAURENCE KENNAWAY (*Biochem. J.*, 1918, **12**, 120—130).—The concentration of acetone substances in the blood in diabetic coma may be equivalent, when reckoned as acetoacetic acid, to that of a $0.03N$-solution; this amount is sufficient to combine with more than one-third of the sodium of the plasma. H. W. B.

The Existence of Creatinine and Creatine in the Blood in Normal and Pathological Cases. III. Normal Cases, especially in Old Age. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **87**, 1—22).—The creatinine and creatine content in the blood of individuals of varying ages is tabulated according to the ages.

S. B. S.

The Presence of Phosphates in Human Blood-serum. VI. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **87**, 237—247).—A general summary of results dealing with the acid soluble and residual phosphorus in pathological cases, with the relationship between the lipoid and residual phosphorus, and with lecithinæmia in cases of mental diseases. S. B. S.

Chemical Studies in Physiology and Pathology. IV. Hæmolysis. The Complement. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **87**, 36—76. Compare this vol., i, 241). —The authors develop further their conceptions as to the chemical and physical nature of proteins and the mode of action of proteoclastic ferments.

Hæmolysis, according to their views, depends on the destruction of the semipermeable structure of the membrane of the blood-corpuscles. This can be brought about either by mechanical or chemical means. Included in the former are such methods as the sudden transference of the corpuscles to hyper- or hypo-tonic solution, drying, etc. The chemical hæmolytics act either directly as solvents (especially for the lipoid constituents) or they act as hydrolytic reagents on lipoids or proteins, or on both.

The agglutination of erythrocytes follows the same laws as that of bacteria and other "hydrophil" suspensions, and is connected intimately with the hydrophil capacity of the surfaces.

In the action of the complement, two functions are to be distinguished. (1) That of the "middle-piece," which is a globulin precipitation and renders the surface of the blood cells more capable

of taking up certain degradation products of the serum ("per-sensitisation") which form the constituents of the "end-piece." (2) The "end-piece" function consists in the direct solvent or hydrolytic action of the degradation products contained in the albumin fraction. The chief influences which inhibit or destroy the complement action can be ascribed to actions on the globulins, which render these substances too stable and less liable to be precipitated, such as dilution with water, Brand's modification, addition of citrates, oxalates, acids, alkalis, action of heat, etc. Other "anti-complement" actions consist in removal of the globulins from the serum, such as addition of precipitants of globulins, bacteria, agar, and cobra-poison. S. B. S.

Action of Symbiotic Bacteria on the Constituents of Fats. HENRI BIERRY and PAUL PORTIER (*Compt. rend.*, 1918, **166**, 1055—1057).—The symbiotic bacteria isolated from the testicle of a pigeon oxidise glycerol in a yeast bouillon, giving a C_3 sugar, glycerose, but the same organisms in a chemically definite medium containing asparagine, glycerol, nitrate, etc., give no trace of dihydroxyacetone. The symbiotes also cause β-oxidation, acetaldehyde and acetone being obtained from β-hydroxybutyric acid and from butyric acid. W. G.

Importance of the Ketonic Function in Metabolism. Its Creation by Symbiotic Bacteria. PAUL PORTIER and HENRI BIERRY (*Compt. rend.*, 1918, **167**, 94—96. Compare preceding abstract).—It is shown that the symbiotes of mammals and birds are capable, in suitable medium, of converting pentoses, hexoses, disaccharides, and certain polyhydric alcohols into acetylmethylcarbinol, amongst other products. On the other hand, when the conditions of the medium are suitable, they are capable of synthesising polysaccharides, the yield of the latter being greatest when a ketose is present. It is also noted that the production of a polysaccharide by symbiotic action is always accompanied by the production of alkalinity in the medium. W. G.

Sugar Metabolism and Diabetes. H. McGUIGAN (*J. Lab. and Clin. Med.*, 1918, **3**, 319—337; from *Physiol. Abstr.*, 1918, **3**, 182—183).—Attention is directed to the variations found in the reducing substances in the blood caused by differences in the concentration of the alkali, and of salts when the latter have been used for precipitating the proteins. There is apparently no difference in the condition of sugar in the blood in normal and in diabetic cases. Observations on utilisation of sugar in muscular contraction, on effect of vascular changes in the liver on glycogenolysis, and on peptone hypoglycæmia are recorded. S. B. S.

The Water-soluble Accessory Growth-promoting Substance. II. Its Influence on the Nutrition and Nitrogen Metabolism of the Rat. JACK CECIL DRUMMOND (*Biochem. J.*, 1918, **12**, 25—41).—When rats are fed on an artificial diet deficient

in the water-soluble accessory substance, the only apparent deviation from the normal nitrogen metabolism is the appearance of creatinuria, accompanied by a slow wasting of the skeletal muscles. The food consumption is low; it may be increased by the addition of flavouring agents, such as meat extract, to the diet, but unless this agent contains the water-soluble accessory, growth does not occur. The addition to the inadequate diet of extracts containing the water-soluble substance causes a greatly increased intake of food, immediately followed by growth. The amount of growth is, within certain limits, proportional to the amount of accessory substance added, provided that the diet is adequate in other respects. The length of time that a rat is able to maintain itself on a diet deficient in the water-soluble substance without suffering a serious loss of body-weight is directly proportional to the age at which the restriction is imposed. Actively growing animal tissues (embryos, tumours) do not contain appreciable amounts of the water-soluble accessory substance; desiccated pituitary, thyroid, and thymus glands, and testicular and ovarian tissues, are also deficient in this respect. H. W. B.

The Utilisation of Yeast in the Animal Organism. EMERICH SCHILL (*Biochem. Zeitsch.*, 1918, **87**, 163—175).—Experiments on dogs indicated that the proteins of yeast can not only be resorbed by the organism, but can produce a positive nitrogen balance. About half the chemical energy of yeast can be utilised by the organism. S. B. S.

Influence of the Species of Animal on the Toxicity and Mode of Utilisation of Alimentary Proteins. E. MAIGNON (*Compt. rend.*, 1918, **167**, 91—94).—Feeding experiments, similar to those carried out with white rats, have been performed with dogs, the same three proteins (egg-albumin, fibrin, casein) being used. The dog accommodates itself much better than the rat to a purely protein diet, and was able to retain its weight for a considerable time on casein or meat powder alone. On the other hand, casein is much more toxic for dogs than for rats. Whereas rats on this diet died from exhaustion of their reserves, dogs died undoubtedly as a result of toxic action. The toxicity of a given protein varies from one species of animal to another apparently inversely as the ease with which the animal can transform the protein into fat. W. G.

Digestion of the Proteins of Cooked Meat in Dogs with Ligatured Carotid Arteries. EDGARD ZUNZ (*Biochem. J*, 1918, **12**, 42—59).—After the ligature of the carotids, a meat meal is retained in the stomach for a longer time than occurs in the normal animal, due, apparently, to an altered blood supply to, or innervation of, the stomach produced by the operation. H. W. B.

Origin of the Conception of Physiologically Balanced Salt Solutions. JACQUES LOEB (*J. Biol. Chem.*, 1918. **34**, 503—504).—The author claims to have originated the conception

of physiologically balanced salt solutions (*Amer. J. Physiol.*, 1899—1900, **3**, 445). H. W. B.

Active Substances in Glands with Internal Secretions.
ERNST BERLIN (*Zeitsch. Biol.*, 1918, **68**, 371—390).—Extracts of spleen contain, besides choline, a substance which exerts a powerful action on the muscles of the uterus and intestine. The latter substance is not β-amino-4-ethylglyoxaline. Both choline and the unknown substance occur also in a commercial extract of spleen called hormonal. H. W. B.

The Genesis of Thiocyanic Acid in Animals. S. DEZANI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 113—128; from *Physiol. Abstr.*, 1918, **3**, 164).—Thioacetamide does not give rise to thiocyanic acid in the dog, and thus the hypothesis of Röhmann as to its genesis from fatty nitriles through the corresponding thioamides or thioamidic acids is not substantiated. In the dog, the ingested nitrile is partly transformed into thiocyanic acid and partly eliminated as such. The remainder is transformed into products which have not yet been identified. S. B. S.

Anti-scorbutic Value of Cow's Milk. HARRIETTE CHICK, ELEANOR MARGARET HUME, and RUTH FILBY SKELTON (*Biochem. J.*, 1918, **12**, 131—153).—Guinea-pigs grow when fed on a diet of oats and bran with milk which has been heated at 120° under pressure, but they rapidly develop scurvy. If some fresh, unheated milk is added to the diet, scurvy may appear sooner or later, according to the amount of milk in the daily ration. By greatly increasing the amount of milk so that the daily ration exceeds 100 c.c., the onset of scurvy is entirely prevented. Milk is therefore relatively poor in the anti-scorbutic accessory substance, and it is most essential that, for the prevention of scurvy, infants fed on milk which has been previously heated or dried should also be given orange juice, raw swede juice, or similar material rich in the anti-scorbutic vitamine. A connexion between scurvy and chronic constipation (McCollum and Pitz, A., 1917, i, 604) is not confirmed.
H. W. B.

Milk as a Source of Water-soluble Vitamine. THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY and ALFRED J. WAKEMAN] (*J. Biol. Chem.*, 1918, **34**, 537—551).—The authors find that vigorous growth of rats does not occur on diets in which the water-soluble vitamine is supplied by milk unless considerable quantities of the milk are consumed. Milk does not contain, therefore, as much water-soluble vitamine as Hopkins's experiments (A., 1912, ii, 779) would lead one to expect (compare preceding abstract). H. W. B.

Carbon Dioxide Content of Urine. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1918, **34**, 569—575).—The total amount

of free and combined carbon dioxide passed in the urine in twenty-four hours by a normal person may vary from 4 to 400 c.c., according to the nature of the ingested food. Vegetable food increases and animal food decreases the output of carbon dioxide in the urine. The carbon dioxide present in the urine varies inversely, although not proportionately, with the hydrogen ion concentration.

H. W. B.

Creatine and Creatinine. VIII. Alleged Exogenous Origin of Urinary Creatine in the Protein of the Diet. WILLIAM C. ROSE, J. STERLING DIMMITT, and H. LEIGH BARTLETT (*J. Biol. Chem.*, 1918, **34**, 601—612).—The authors find that the ingestion of diets excessively high in protein fails to induce the excretion of creatine in normal men and women. The theory that creatine has an exogenous origin in the protein of the diet is not confirmed (compare Denis, Kramer, and Minot, A., 1917, i, 526).

H. W. B.

Examination of the Fæces of Rabbits Fed on a Diet of Cabbage for the Occurrence of a Phytosterol. The Phytosterols in Cabbage Seeds and Grass Fruits. MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 154—159).—The fæces of rabbits fed on cabbage do not contain a typical phytosterol, but a trace of a substance resembling coprosterol, melting at 102°, may be detected. Cabbage seeds contain a relatively large amount of phytosterols similar to those present in rape oil. Grass fruits contain a trace of phytosterol, together with chortosterol (compare Dorée and Gardner, A., 1908, ii, 514).

H. W. B.

Biochemistry and Chemotherapy of Tuberculosis. XVI. Pharmacology and Toxicology of Copper Salts of Amino-acids. HARRY L. HUBER (*J. Pharm. Exp. Ther.*, 1918, **11**, 303—329).—The copper salts of leucine, glycine, and glutamic acid produce exactly the same physiological effects as copper sulphate when administered in various ways to guinea-pigs and rabbits.

H. W. B.

Effect of Intravenous Injections of some Sodium Salts with Special Reference to the supposed Toxicity of Sodium Phosphate. ISIDOR GREENWALD (*J. Pharm. Exp. Ther.*, 1918, **11**, 281—301).—The intravenous injection of neutral solutions of sodium chloride, sulphate, and phosphate into dogs produces changes in the volume, osmotic pressure, and reaction of the blood, and results in disturbances of the normal relations between the various ions of the blood and tissues. It is to these physical factors rather than to a direct toxic action of the phosphate ion that the ill-effects observed after the administration of sodium phosphate solutions are to be ascribed (compare Binger, A., 1917, i, 677). Muscle twitching, tetany, and violent convulsions may be produced by the injection of the chloride and sulphate, as well as of the

phosphate of sodium, and seem to be dependent more on the sodium than on the phosphate ion, since a balanced solution containing high concentrations of sodium, potassium, and calcium in certain fixed proportions may be introduced without producing any ill-effects. The injection of sodium salts is followed by the elimination of both potassium and calcium salts in the urine, but whereas the content of calcium in the blood and serum falls, that of potassium remains unchanged.   Similarly, the injection of either sodium sulphate or phosphate, as well as of the chloride, occasions an increased elimination of chlorides in the urine, probably due to differences in the permeability of the kidneys to the different salts.   H. W. B.

Metabolism of the Mustard Oils. W. H. PETERSON (*J. Biol. Chem.*, 1918, **34**, 583—600).—The addition of allylthiocarbimide, 0·2 to 0·4 gram per day, and allyl sulphide, 0·5 to 1 gram per day, to the starchy diet of a pig produces a gradual rise in the total sulphur excreted in the urine, which persists for ten to twelve days after the ingestion of these compounds has ceased.   This points to a very slow metabolism and the inability of the body to dispose readily of them.   These compounds are not oxidised during their passage through the body, but are converted into a non-volatile, less toxic substance which has not been identified.   From 40 to 70% of the sulphur in the ingested compound can be subsequently recovered from the urine, the remainder being probably eliminated in the form of volatile compounds through the lungs and skin.   The two sulphur compounds are practically completely absorbed, scarcely a trace being excreted in the fæces.

H. W. B.

The Behaviour of Urotropine and Formaldehyde in the Organism. E. SALKOWSKI (*Biochem. Zeitsch.*, 1918, **87**, 143—162). —The author has investigated the various reactions for formaldehyde with the object of detecting this substance in the presence of much larger quantities of urotropine.   The only quite satisfactory reaction for this purpose was found to be that of Jorissen as modified by Vanino (with phloroglucinol and sodium hydroxide, A., 1899, ii, 703).   Solutions of urotropine cannot be kept without decomposition for any great length of time; they are somewhat more stable in the presence of sodium carbonate (0·1—1%), and such solutions can be kept without appreciable change for a week. In the presence of slight amounts of acid, solutions alter from day to day.   There is, apparently, a scission of formaldehyde from urotropine, which takes place in the stomach.   Examination of the urine after ingestion of urotropine reveals the fact that it is partly excreted unchanged, and partly oxidised to formic acid.

S. B. S.

Atophan and some of its Derivatives. LUISE ROTTER (*Zeitsch. exp. Path. Ther.*, 1917, **19**, 176—197; from *Physiol. Abstr.*, 1918, **3**, 194—195).—Atophan (2-phenylcinchonic acid) is

toxic to cold-blooded, but not to warm-blooded animals. It para-
lyses both the central nervous system and the nerves of the heart
of frogs, and the heart generally stops beating in systole. Atophan
owes its activity to the linking up of a phenyl group to a quinoline
nucleus, as quinolinecarboxylic acid is almost inactive. Other sub-
stitution products were investigated, and generalisations as to
chemical constitution and pharmacological action are made. No
substance antagonistic in action to atophan was discovered. After
ingestion by the mouth in man, hydroxyphenylquinolinecarboxylic
acid is excreted in the urine, together with an increased amount
of uric acid. To the former the increased output of uric acid is
ascribed, as such an increased excretion can be produced by its
direct administration.   S. B. S.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Cyanohydrins on Ferments and Bacteria.

MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **87**, 129—134).—The action of the urease of soya bean is strengthened by the presence of the cyanohydrin of acetaldehyde, but inhibited by the corresponding propaldehyde derivative. Both compounds inhibit strongly the ferment formation by bacteria, whilst they exert only a very moderate deleterious action on the bacteria themselves.

S. B. S.

The Degradation of Tyrosine by Bacterium coli phenologenes, and the Composition of Human Urines containing Phenol.

M. RHEIN (*Biochem. Zeitsch.*, 1918, **87**, 123—128).— Phenol is formed by *Bacterium coli phenologenes* only from tyrosine and *p*-hydroxybenzoic acid. It was not formed from the following (possible intermediary degradation products of tyrosine): *p*-hydroxyphenylpropionic acid, *p*-hydroxyphenylacetic acid, *p*-hydroxyphenylpyruvic acid, *p*-hydroxyphenylethylamine, *p*-hydroxyphenylethyl alcohol, *p*-hydroxyphenyl-*α*-lactic acid, and *p*-cresol. It appears, therefore, that tyrosine is degraded by attack of the *β*-carbon atom of the alanine chain and simultaneous oxidation. Phenol and *p*-cresol in human urines can be detected readily by the colour reactions with formaldehyde–sulphuric acid and with diazobenzenesulphonic acid in sodium carbonate solutions.

S. B. S.

The Influence of Lactic Acid on Lactic Acid Fermentation.

W. VAN DAM (*Biochem. Zeitsch.*, 1918, **87**, 107—122).—Investigations were made to ascertain whether the stoppage of fermentation by the coccal form of bacteria is due to the action of the hydrion

of the lactic acid produced or to the undissociated molecule. The conclusion is drawn that the stoppage is due to both. If sodium lactate is added to the whey, further acid formation ceases when the concentration of the undissociated molecule reaches $0\cdot01N$. In such cases, the final hydrion concentration fails to reach the toxic amount of about 10×10^{-5}. If hydrochloric acid is added to the whey before inoculation, so much lactic acid is formed as to bring the final hydrion concentration to $10—20 \times 10^{-5}N$. In this case, the amount of undissociated lactate remains below the toxic amount. Attention is directed to the fact that certain conclusions of other authors as to the value of the nitrogenous nutrients are vitiated by their failing to take into account their buffer action.

S. B. S.

The Bacterial Degradation of d-Tyrosine, with Special Reference to the Stereochemical Configuration of the Degradation Products. M. TSUDJI (*Acta. Schol. Med. Kyoto,* 1918, **2**, 115—123; from *Physiol. Abstr.,* 1918, **3**, 165).—A continuation of previous work (A., 1917, i, 679). Although in degradation of the *dl*-form, the *l*-form is rapidly acted on, the *d*-form does not remain entirely intact, and can be slowly broken down by *Bacterium subtilis* or *B. proteus* in media containing phosphates. The same products are obtained whether *dl*-, *d*-, or *l*-tyrosine is used as substrate, namely, d-p-hydroxyphenyllactic acid by the action of *B. proteus* and the corresponding *l*-acid by the action of *B. subtilis*. It is suggested that in both cases the inactive p-hydroxyphenylpyruvic acid is formed as an intermediate product.

S. B. S.

By-products of the Fermentation of Cabbage. V. E. NELSON and A. J. BECK (*J. Amer. Chem. Soc.,* 1918, **40**, 1001—1005).—The fermented cabbage examined was the ordinary commercial material, "sauerkraut." The volatile acidity represented from 25—50% of the total acidity. The volatile acids consisted of acetic and propionic acids, no higher acids being present, although in two cases formic acid was isolated. The fixed acidity was in all probability due to an inactive form of lactic acid. Alcohols were present to the same extent as volatile acids, and consisted entirely of ethyl and propyl alcohols. Esters, present only in small amount, contributed an essential part in the flavour and aroma. Mannitol was present in the fermented cabbage to the extent of $2\cdot0—2\cdot5\%$, and must have arisen from bacterial decomposition of the carbohydrates, since none is present in the natural plant.

W. G.

Formation of Esters of Phosphoric Acid during Alcoholic Fermentation. ALEXANDRE LEBEDEV (*Biochem. J.,* 1918, **12**, 87—92).—By treatment of a fermenting solution containing yeast, sucrose, and phosphates with alcohol, a mixture of esters of phosphoric acid can be isolated which yields an *osazone,* $C_{33}H_{37}O_7N_8P$;

this appears to be the osazone of an ester of phosphoric acid containing one molecule of the latter combined with a molecule of hexose and a molecule of triose. The osazone or mixture of osazones melts at 142—144°; a p-*bromophenylosazone*, m. p. 141—142°, and a *barium* salt have also been isolated, and in each case have been found to possess different properties from those associated with the corresponding compounds of ordinary hexose phosphate.

<div align="right">H. W. B.</div>

Fermentation of Glyoxylic Acid. ALEXANDRE LEBEDEV (*Biochem. J.*, 1918, **12**, 81—86).—Dried yeast (Lebedev) decomposes glyoxylic acid, forming carbon dioxide and acetaldehyde.

<div align="right">H. W. B.</div>

Nature of the Proteolytic Enzyme of Yeast. NICOLAUS IVANOV (*Biochem. J.*, 1918, **12**, 106—119).—When autolysing yeast is treated with potassium hydrogen phosphate, the decomposition of protein is accelerated, resulting in an increased production of peptones. A similar accumulation of peptones occurs when the autolysis proceeds at a relatively high temperature (54°). If, however, the autolysis proceeds in an alkaline medium, the decomposition of the proteins is inhibited, whilst a large production of amino-acids is obtained. Apparently the proteolytic enzyme of yeast is composed of two factors, a protease acting on proteins and forming peptones, and a peptase transforming the peptones into amino-acids. By varying the conditions in the manner indicated above, it is possible to inhibit the action of one factor without interfering with the activity of the other. It is probable that the peptase of yeast is identical with animal erepsin.

<div align="right">H. W. B.</div>

Differential Behaviour of the Antineuritic and Anti-scorbutic Factors towards Adsorbents. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 93—105). —The anti-neuritic substance present in autolysed yeast is quantitatively adsorbed by fuller's earth or by dialysed iron. When a mixture of equal volumes of autolysed yeast (containing the anti-neuritic factor) and orange juice (containing the anti-scorbutic factor) is treated with fuller's earth, the anti-neuritic factor is entirely removed, whilst the anti-scorbutic activity remains unaltered. So far, it has not been found possible to separate the anti-neuritic substance in an active form from the fuller's earth adsorption complex.

<div align="right">H. W. B.</div>

The Formation of Nitrites from Nitrates in Aqueous Solution by the Action of Sunlight and the Assimilation of the Nitrites by Green Leaves in Sunlight. BENJAMIN MOORE (*Proc. Roy. Soc.*, 1918, [*B*], **90**, 158—167).—Dilute solutions of nitrates exposed either to sunlight or to a light-source rich in light energy undergo conversion into nitrites. If leaves are immersed in the nitrate solutions, comparatively little nitrite accumulates.

Nitrates taken up by plants from soil would, in the presence of sunlight, be converted into nitrites, which are more reactive, and it is held by the author that the early stages of synthesis of nitrogenous compounds are carried out by the green leaf, aided by sunlight. Rain-water collected for a considerable time contains no nitrites, all having been oxidised to nitrates, but if exposed to light for a few hours, a strong reaction for nitrites is obtained. Freshly-collected rain-water or dew contains both nitrates and nitrites. Air bubbled through nitrite- and nitrate-free water gives a reaction, when the water is tested afterwards for nitrates and nitrites showing the presence of both forms of oxides of nitrogen in air. The "ozone" odour in air is probably due to oxides of nitrogen formed by the action of sunlight rich in ultra-violet light in the upper layers of the atmosphere on air and water-vapour.   S. B. S.

The Carbohydrate Nutrition of Plants.   T. BOKORNY (*Biol. Zentr.*, 1916, **36**, 385—403; from *Physiol. Abstr.*, 1918, **3**, 208). —De-starched *Spirogyra* in water free from carbon dioxide can form starch in light from lactose, galactose, raffinose, dextrose, methyl alcohol, glycerol, ethyl acetate in the presence of monohydrogen dipotassium phosphate, and formaldehyde. It does not form starch under similar conditions from lævulose, sorbose, arabinose, xylose, rhamnose, acetone, and a number of other organic substances. Yeasts can apparently use methyl alcohol as a source of carbon only in the presence of dextrose or sucrose.   S. B. S.

Metachromatin and the Phenolic Compounds of the Plant Cell.   A. GUILLIERMOND (*Compt. rend.*, 1918, **166**, 958—960). —The substance existing in the higher plants described by Dangeard as metachromatin is not comparable with the metachromatin of fungi. It is a phenolic compound capable of being converted into anthocyanin, which is formed thus by a chemical transformation of this compound, and not by fixation on it. The presence of this compound in the vacuole is not general, only being localised in special tissues.   W. G.

The Constitution of a Plant Salt coming from the Cameroons.   A. LACROIX (*Compt. rend.*, 1918, **166**, 1013—1015. Compare Dybowski and Demoussy, *ibid.*, 1893, **116**, 398).—The salt is obtained by lixiviation of the plant ashes of a grass, which is probably *Panicum crus Galli*, L. Its principal ingredients are: $Cl = 42.81\%$; SO_3, 5.24%; K_2O, 56.73%; Na_2O, 1.63%; CaO, 1.19%, and a little magnesia, silica, and organic matter. Mineralogically, it is found to contain sylvine, sodium chloride, magnesium chloride, syngenite, and glaserite.   W. G.

Transformation of Inulenin by Autohydrolysis in the Tubercles of Asphodels.   E. COUVREUR (*Compt. rend. soc. biol.*, 1918, **81**, 40—41; from *Physiol. Abstr.*, 1918, **3**, 201).—Inulenin differs from inulin in its mode of crystallisation in fine needles. Maltose is not present in the tubercles of the fresh tissues of

Asphodel crasiferus and *A. microcarpus*, but appears after they have been triturated with water, and can be identified by the osazone test.   S. B. S.

Chemistry of the Cotton Plant, with Special Reference to Upland Cotton. ARNO VIEHOEVER, LEWIS H. CHERNOFF, and CARL O. JOHNS (*J. Agric. Research*, 1918, **13**, 345—352. Compare Perkin, T., 1909, **95**, 1855, 2181; 1916, **109**, 145).—Quercimeritrin and *iso*quercitrin, previously isolated by Perkin (*loc. cit.*) from other types of cotton plant, have now been found in Upland cotton (*Gossypium hirsutum*). The leaves and flowers, with petals removed, contain quercimeritrin, whilst the petals contain this and *iso*quercitrin. Gossypitrin and gossypetin, which have been isolated from other types of cotton, could not be found in Upland cotton. The authors also isolated an ethereal oil from *G. hirsutum* differing from that found by Power and Browning (compare A., 1914, i, 1163) in the root bark of *G. herbaceum*. The new oil, present only to the extent of 0·0015 to 0·0071%, distils mainly between 200° and 300°, and leaves a black, empyreumatic residue; it is attractive to the boll weevil.   W. G.

Chemistry and Histology of the Glands of the Cotton Plant, with Notes on the Occurrence of Similar Glands in Related Plants. ERNEST E. STANFORD and ARNO VIEHOEVER (*J. Agric. Research*, 1918, **13**, 419—436).—For the most part botanical. The glands in portions of the plant which are exposed to light are surrounded by an anthocyanin-bearing envelope of flattened cells, and contain quercetin, probably partly or wholly in the form of its glucosides, quercimeritrin or *iso*quercitrin, ethereal oils, resins, and perhaps tannins. The glands not normally exposed to light contain gossypol, and are surrounded by cells not containing anthocyanins. Gossypol is formed in the glands of the developing corolla, and on their exposure to light it is replaced by quercimeritrin. In the unfolding cotyledons, gossypol is changed, probably through oxidation, without the formation of quercimeritrin.   W. G.

The Active Glucosides of Digitalis Leaves of Various Origin and some Commercial Galenicals Compared Quantitatively. ERNST MEYER (*Arch. exp. Path. Pharm.*, 1917, **81**, 261—288).—Kraft's gitalin (A., 1911, i, 734; 1912, i, 373) is very readily soluble in chloroform, but not in water; yet it cannot be extracted by chloroform from perfectly dry leaves, or from a cold water leaf-extract which has been completely dried over sulphuric acid. The addition of very little water to the dried extract, however, again renders the gitalin soluble in chloroform, and hence it can also be extracted from fresh leaves by chloroform. The extraction of gitalin from the leaves by cold water is attributed to the presence of tannins (see following abstract), from which the gitalin may be separated by chloroform.

Of commercial preparations, digalen and its copy digipan contain gitalin, and are probably cold water extracts. Digipuratum and digitalysatum contain only a portion of the gitalin and correspond with hot water infusions.   G. B.

The Amount of Substances with a Digitalis Action in Oleander Leaves and the manner of their Natural Occurrence (Tannoid Question). WALTHER STRAUB (*Arch. exp. Path. Pharm.*, 1918, **82**, 327—343).—The activity of oleander leaves is about 2·5 times as great as that of digitalis leaves. Two crystalline active glucosides have been obtained by Böhringer & Söhne. One of these, *oleandrin* (C 67·85%, H 7·74%), is very active, about as much so as amorphous *k*-strophantin, and is almost insoluble in water when pure. Amorphous active glucosides are also present in larger amount. Nevertheless, the whole of the active substances are readily extracted by cold water, and this solubility seems due to the large amount of a phenolic glucoside present in the leaves, which is not a true tannin. This substance is coloured green by ferric chloride, and is also present in digitalis leaves, but in smaller amount, so that the whole of the active substances of digitalis are not extracted by cold water. (See preceding abstract.)   G. B.

Action of Normal Salts on Humus and other Experiments on Soil Acidity. LOUIS J. GILLESPIE and LOUIS E. WISE (*J. Amer. Chem. Soc.*, 1918, **40**, 796—812. Compare Gillespie, A., 1916, i, 303; Sharp and Hoagland, *J. Agric. Research*, 1916, **7**, 123).—The addition of solutions of chloride of sodium, potassium, or barium to humus causes a large increase in the hydrogen ion concentration as measured electrometrically, but as similar although smaller effects are observable in the action of potassium chloride on true solutions in the absence of humus or of undissolved solid matter, great care is required in drawing conclusions as to the mechanism of the process in the case of humus. At equivalent concentrations, barium chloride exerted the greatest influence on the electrometric potential of humus preparations. Considerable precaution is necessary in using litmus for the detection of acidity of soils, because even in very dilute solutions of hydrochloric acid the result is largely influenced by the "buffer" action of the solution under test. It is improbable that soils can act on litmus solely by virtue of their adsorptive power, and the difference in the effect of a moistened soil and of its aqueous extract on litmus may be due to the sparing solubility of the acidic organic substances of the soil. It is inadvisable at present to attempt broad general explanations of the cause of soil acidity, but the investigations with the hydrogen electrode and suitable indicators supply ample evidence of the common occurrence and wide distribution of truly acid soils in the United States.   D. F. T.

Organic Chemistry.

Nature of the Kolbe Electrochemical Synthesis of Hydrocarbons. FR. FICHTER and EDUARD KRUMMENACHER (*Helvetica Chim. Acta*, 1918, **1**, 146—166).—The authors discuss the two theories put forward to explain the mechanism of the Kolbe hydrocarbon synthesis, and draw the conclusion that the oxidation theory is more in accord with fact than the theory based on the ionic hypothesis. It is shown that peroxides are produced by electrochemical oxidation, on platinum anodes, of solutions of saturated fatty acids and their salts. Since these peroxides may be produced by the action of hydrogen peroxide on acid anhydrides, it is to be assumed that the separation of the anhydride is the first step in the hydrocarbon synthesis. The anhydride is then anodically oxidised, with the formation of a very unstable peroxide. The peroxide is then decomposed by the relatively high temperature of the anode, with the formation of the hydrocarbon, thus: $R \cdot CO_2 Na \longrightarrow (RCO)_2 \cdot O + O \longrightarrow (RCO)_2 \cdot O = O \longrightarrow R \cdot R + 2CO_2$, or a side reaction may also occur, thus: $(R \cdot CO)_2 O = O \longrightarrow R \cdot CO_2 \cdot R + CO_2$. When the peroxides are decomposed by heat, there is also a considerable amount of methane produced in addition to the expected hydrocarbon.

These considerations are adapted to the formation and decomposition of organic peracids. Organic peracids may be prepared by the action of hydrogen peroxide on both acids and anhydrides, consequently the formation of these substances electrolytically on the anode does not necessarily demand the intermediary formation of the anhydride. A further possibility also arises from the fact that peracids may be hydrolysed to peroxides. The peracids also decompose at the anode surface, giving carbon dioxide and an alcohol, $R \cdot CO_3 H \longrightarrow R \cdot OH + CO_2$, or carbon dioxide and an unsaturated hydrocarbon, $C_n H_{2n+1} \cdot CO_3 H = C_n H_{2n} + CO_2 + H_2O$.

By the electrolysis of sulphonediacetic acid or its salts, the products are carbon dioxide and sulphuric acid, and not the expected product, diethylene disulphone. J. F. S.

Determination of the Normal Density of Ethylene. T. BATUECAS (*Anal. Fis. Quim.*, 1918, **16**, 258—281; *Helvetica Chim. Acta*, 1918, **1**, 136—141).—The mean of twenty-one determinations with samples of ethylene prepared from ethyl alcohol by phosphoric acid, boric acid, sulphuric acid, and alumina gave for the normal density the value $L_0 = 1 \cdot 26031$ grams. A. J. W.

Silver Acetylide. JOHN EGGERT (*Zeitsch. Elektrochem.*, 1918, **24**, 150—154. Compare A., 1918, ii, 228).—The amount of gaseous product produced by the detonation of silver acetylide depends on the method of preparation. Silver acetylide prepared

from an acid silver nitrate solution evolves about ten times the
volume of gas, on detonation, as does material prepared in
ammoniacal solution, neutral solution, or in solution of hydrofluoric
acid. The material prepared in nitric acid solution contains 78·5%
of silver, and the gaseous product of detonation consists of a mix-
ture of carbon monoxide, carbon dioxide, methane, hydrogen,
nitrogen, nitric oxide, and water vapour. The material prepared
in 2% ammoniacal solution contains 89·5% of silver, and the product
of detonation consists of carbon monoxide, carbon dioxide, methane,
hydrogen, and water vapour. The analyses show that the product
from nitric acid consists of 57% of silver acetylide and 43% of silver
nitrate, whilst that from ammonia consists of 86% of silver acetylide
and 14% of silver hydroxide.   J. F. S.

**Methods of Formation of Chlorohydrins. I. Glyceryl
Chlorohydrins.** L. SMITH (*Zeitsch. physikal. Chem.*, 1918, **92,**
717—740).—The author has found that the velocity constants for
the hydrolysis of chlorohydrins steadily decrease as the action pro-
ceeds and has attributed this action to the presence of two (or more)
isomerides in the material employed. The nature of the chloro-
hydrin prepared by the various methods is not well investigated,
and the usual methods are not very suitable for recognising these
compounds in mixtures. The rate of hydrolysis by alkali hydroxides
can be used for this purpose, and from the rate with which the
velocity constant changes it is possible to state which isomerides
are present. Using this method, the products obtained by the
various methods for the preparation of glyceryl chlorohydrin have
been examined. (1) Glyceryl monochlorohydrin, prepared from
*epi*chlorohydrin, consists entirely of α-monochlorohydrin.
(2) Monochlorohydrin from glycerol by the action of hydrogen
chloride is a mixture of the α- and β-compounds containing a large
excess of the α-derivative. (3) By the action of hypochlorous acid
on allyl alcohol, a mixture of the α- and β-chlorohydrins is pro-
duced which consists mainly of the β-compound. (4) The mono-
chlorohydrin produced by the action of hydrogen chloride consists
of a mixture of 85—90% of the α-compound and 10—15% of the
β-compound. A number of experiments are described which are
designed to separate the constituents of the mixtures. (5) Glyceryl
dichlorohydrin, prepared by the action of chlorine on allyl alcohol,
contains only traces of the αγ-compound. (6) The product of the
action of hydrogen chloride on *epi*chlorohydrin contains nothing
but the pure αγ-compound. (7) The product of the action of
hypochlorite on allyl alcohol contains about one-third of its weight
of αγ-dichlorohydrin. The whole of the hydrolytic experiments
were carried out with both baryta and sodium hydroxide.
                                                        J. F. S.

**Methods of Formation of Chlorohydrins. II. Propylene
Chlorohydrins.** LENNART SMITH (*Zeitsch. physikal. Chem.*, 1918,
93, 59—88. See preceding abstract).—The author has prepared
the propylene chlorohydrins by various methods, and has examined

the products by the kinetic method (*loc. cit.*) with the object of ascertaining their composition, and so deciding the best methods for preparing the different isomerides. (1) The product of the action of water on allyl chloride gives pure propylene α-chlorohydrin; (2) by the action of sulphur chloride on propylene glycol, a product containing 25% of the β-compound and 75% of the α-compound is obtained; (3) propylene glycol treated with hydrogen chloride yields more β-chlorohydrin than in case (2); (4) propylene oxide treated with hydrogen chloride yields mainly the α-compound with not inconsiderable quantities of the β-compound; (5) the action of hypochlorite on propylene yields a mixture of the products. Henry's method (A., 1903, i, 725) for converting the α-chlorohydrin into β-chlorohydrin has been examined, and it is shown that the product consists mainly of the α-derivative.

<div align="right">J. F. S.</div>

Autoxidation of some Derivatives of Thioncarbonic Acid.

O. BILLETER and B. WAVRE (*Helvetica Chim. Acta*, 1918, 1, 167—174).—Compounds containing the group C:S, and particularly those of the types $CS(OR)(SR)$, $CS(OR)_2$, $CSCl(OR)$, and thiocarbonyl chloride, $CSCl_2$, are phosphorescent and rapidly absorb oxygen, being thereby oxidised. These substances also emit a phosphorescent vapour. The oxidation occurs only in the presence of a catalyst such as a hydroxide of the alkali or alkaline earth metals, alkali carbonates, oxides of zinc or magnesium, and ammonia. Ethyl xanthate in the presence of excess of $N/10$-ammonia solution rapidly absorbs oxygen, and about 90% of the sulphur present is converted into sulphuric acid; some of the compound, $OEt \cdot CO \cdot SEt$, is also produced. Methyl methylxanthate in the presence of *N*-ammonia is oxidised very rapidly, the sulphur being oxidised to thiosulphate, sulphite, trithionate, and sulphate, whilst hexamethylenetetramine is also formed. Methyl thioncarbonate, $CS(OMe)_2$, is rapidly oxidised, 38% of the sulphur being regained as sulphuric acid, whilst the rest appears as thiosulphuric acid, sulphurous acid, and a little trithionic acid. The ethyl ester, $CS(OEt)_2$, does not undergo autoxidation in the presence of pure oxygen, but with air 40% of the ester is oxidised and 14% of the sulphur appears as sulphuric acid, whilst the rest is obtained as thiosulphuric acid, sulphurous acid and a trace of trithionic acid. The chloro-ester, $CSCl \cdot OMe$, is oxidised so rapidly that in the first half minute 83% of the theoretical quantity of oxygen is absorbed, 16·9% of the sulphur is oxidised to sulphuric acid, and the residue to sulphurous acid. Thiocarbonyl chloride is very rapidly attacked, but only about 30% is oxidised normally, the residue being absorbed by the ammonia to form ammonium thiocyanate and sulphur. J. F. S.

Some Metallic Salts and Complex Metallic Derivatives of the Cyanocarboxylic Acids and their Esters. II. LIZZIE PETTERSON-BJÖRCK (*J. pr. Chem.*, 1918, [ii], **97**, 51—58).—An

<div align="right">*t* 2</div>

extension of the earlier paper (A., 1913, i, 27) giving a description of the cobalt and silver salts of cyanoacetic acid and of the platinum derivatives of methyl and ethyl cyanoacetate.

Cobalt cyanoacetate, $(CN \cdot CH_2 \cdot CO_2)_2Co, H_2O$, obtained by the action of cyanoacetic acid on an aqueous suspension of cobalt hydroxide, forms pale red needles, the red aqueous solution of which becomes blue on warming. Silver cyanoacetate, prepared by precipitation from potassium cyanoacetate and silver nitrate in aqueous solution, forms colourless needles (compare Meves, *Annalen*, 1867, **143**, 304). By the interaction of barium cyanoacetate and chrome alum, it is possible to obtain green, prismatic crystals of a chromium cyanoacetate analogous to the ferric salt described earlier (*loc. cit.*). When agitated with an aqueous solution of potassium platinochloride, the methyl and ethyl esters of cyanoacetic acid undergo conversion into the compounds $Pt(CO_2Me \cdot CH_2 \cdot CN)Cl_2$ and $Pt(CO_2Et \cdot CH_2 \cdot CN)Cl_2$ respectively, each crystallising in needles. In the course of attempts to obtain platinum derivatives of free cyanoacetic acid, ammonia platinum sulphate, $Pt(NH_3)_2SO_4$, was treated with dilute aqueous cyanoacetic acid, a blackish-violet, crystalline compound being obtained of the composition $(NH_2 \cdot CO \cdot CH_2 \cdot CO_2)_2Pt$.   D. F. T.

Transformation of Methyl α-Elæostearate into Methyl β-Elæostearate. R. S. MORRELL (*J. Soc. Chem. Ind.*, 1918, **37**, 181—182T).—A continuation of the investigation of the properties of thickened drying oils (T., 1918, **113**, 111). The thickened "tung oil" was divided into fractions soluble and insoluble in acetone. The former was converted into the methyl ester by means of sodium methoxide, and this ester on hydrolysis yielded β-elæostearic acid; the same result was obtained from the fraction insoluble in acetone. The cerium salt was prepared from the undistilled ester, and since it was completely soluble in ether, it was evidently the salt of the α-acid. The author concludes, therefore, that the stereoisomeric change occurs during the distillation of the ester.   J. F. S.

The Ethyl Hydrogen Citrates. L. WOLFRUM and JOH. PINNOW (*J. pr. Chem.*, 1918, [ii], **97**, 23—50. See also A., 1915, ii, 679).—When esterified with ethyl alcohol in the absence of a catalyst, citric acid yields a mixture of *s*- and *as*-ethyl dihydrogen and diethyl hydrogen citrates, of which the constitutions can be distinguished by colorimetric comparison of their ionisation constants (compare Palomaa, A., 1912, i, 6). The α-hydroxy-acids predominate in the product, which also contains a small quantity of derivatives of aconitic acid. It is desirable to exclude moisture as completely as possible during the esterification. The constituent esters of the esterification product can be roughly separated by fractional extraction with ether in a Partheil-Rose apparatus, the final purification of the individual hydrogen esters being effected by recrystallisation of a suitable salt, the calcium salt of the

as-ethyl dihydrogen ester, the zinc salt of the *s*-ethyl dihydrogen ester, and the sodium salt of the *s*-diethyl hydrogen ester being selected for this purpose. As the *as*-diethyl hydrogen citrate is more soluble than its isomeride and has little tendency to the formation of crystalline salts, it is necessary to prepare this by an independent method from ethyl citrate; the partial alkaline hydrolysis of ethyl citrate yields only *as*-diethyl hydrogen citrate, and the further partial hydrolysis of this (or of ethyl citrate) yields *s*-ethyl dihydrogen citrate, so that a convenient method of preparation for each of these two esters is thus supplied (compare Pinnow, this vol., ii, 103; also Meyer, A., 1909, ii, 391, 803). The ester formed during the fermentation of citric acid is a mixture of the ethyl dihydrogen citrates.

s-Diethyl hydrogen citrate, needles, m. p. 58—59°, dissociation constant 1·514 at 15°, forms double molecules in ethereal solution; sodium salt, needles, m. p. 144—145°; *silver* salt, needles; *brucine* salt. The partition coefficient of this ester between ether and water was measured. The *as*-diethyl hydrogen citrate resembles the symmetrical isomeride in possessing a bitter taste, but with the exception of the silver salt, needles, m. p. 109·5—110·5°, the salts are amorphous.

s-Ethyl dihydrogen citrate, for which the partition coefficient between ether and water was determined, forms prisms, m. p. 97·5—98·5°; *silver* salt, tablets; basic *lead* salts,
$$2C_8H_{10}O_7Pb,3C_8H_{10}O_7(PbOH)_2$$
and $3C_8H_{10}O_7Pb,C_8H_{10}O_7(PbOH)_2$; *copper* salt,
$$(C_8H_{10}O_7CuOH)_2Cu,5H_2O,$$
greenish-blue prisms. *as*-Ethyl dihydrogen citrate gave a microcrystalline, basic copper salt, $(C_8H_{10}O_7CuOH)_2Cu,2H_2O$, and a zinc salt, $2C_8H_{10}O_7Zn,(C_8H_{10}O_7ZnOH)_2Zn,13H_2O$; its brucine salt could not be resolved into enantiomorphous forms.

Ethyl citrate is generally contaminated by the presence of ethyl aconitate.

The earlier literature with respect to the ethyl hydrogen citrates is largely misleading and untrustworthy.　　　　D. F. T.

Bromination in the α-Position of the Aldehydes of the Fatty Series. ANTONIO MADINAVEITIA and JOSÉ PUYAL (*Anal. Fis. Quim.*, 1918, **16**, 329—337).—The chloro-ethers formed by the action of hydrogen chloride on mixtures of aldehydes and alcohols in equimolecular proportions are converted by bromine at 0° into chlorobromo-ethers, the bromine atom being adjacent to the chlorine. These derivatives are transformed by water into the α-bromoaldehydes, and by alcohols into the corresponding bromoacetals. The following compounds have been prepared: α-chloro-β-bromodiethyl ether, b. p. 64—65°/13 mm.; α-bromoacetal, b. p. 70—72°/20 mm.; methyl α-chloro-β-bromoethyl ether, b. p. 167° (decomp.); *ethyl α-chloro-β-bromoisoamyl ether*, b. p. 94—96°/15 mm.; *α-bromoisovaleraldehyde*, b. p. 55—56°/25 mm.; and the corresponding *diethyl acetal* derivative, $CHMe_2 \cdot CHBr \cdot CH(OEt)_2$, b. p. 105—107°/30 mm.　　　　A. J. W.

A New Form of Methylgalactoside and its Conversion into Octamethyldigalactose and into a Methyldigalactoside. MARY CUNNINGHAM (T., 1918, **113**, 596—604).—The isolation of four galactose penta-acetates (Hudson, A., 1916, i, 546) indicates the possible existence of a modification of galactose analogous to γ-dextrose, and it is now shown that the syrupy form of methylgalactoside obtained from methyl alcohol and galactose at 100° in the presence of a little hydrogen chloride (Irvine and Cameron, T., 1905, **86**, 907) is an ether of the γ-series. On methylation by the silver oxide method, the γ-methylgalactoside ($[a]_D + 12\cdot95°$ in alcohol, $+25\cdot9°$ in water) is converted into tetramethyl γ-methylgalactoside identical with that described previously (Irvine and Cameron, *loc. cit.*), which on hydrolysis yields tetramethyl galactose; this substance at the ordinary temperature undergoes spontaneous polymerisation to *octamethyl γ-digalactose*, $C_{20}H_{38}O_{11}$. On heating methylgalactoside with acidic methyl alcohol, there is obtained an amorphous methyldigalactoside ($[a]_D$ in methyl alcohol, $+85\cdot6°$; in water, $+101\cdot1°$) identical with the substance regarded by Fischer (A., 1895, i, 439) as a methylgalactoside; the result is the same whether the original methylgalactoside is the α-, β-, or γ-form, and it appears probable that in the presence of acidic methyl alcohol any one of these substances gives rise to an equilibrium mixture of all three, the unstable γ-modification then undergoing hydrolysis to give the reactive type of sugar; the product therefore consists of the stable forms of methylgalactoside (α- and β-) united with the unstable γ-form, the constitution being

$$\text{OMe·CH·[CH·OH]}_2\text{·CH·CH(OH)·CH}_2\text{·O·CH·CH·[CH·OH]}_3\text{·CH}_2\text{·OH}$$
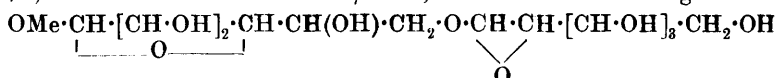
For experimental details, the original should be consulted.

D. F. T.

Application of the Auto-condensation Powers of γ-Sugars to the Synthesis of Carbohydrate Complexes. MARY CUNNINGHAM (T., 1918, **113**, 604—607. Compare preceding abstract).—From the observation that any one of the three methylgalactosides when heated with acidic methyl alcohol gives rise to a mixture of stereoisomeric condensation compounds consisting of the stable α- and β-hexosides united with γ-galactose (preceding abstract), it is possible that similar compounds might be formed by merely dissolving a reducing sugar in this reagent and concentrating the solution. Experiment shows the correctness of this argument, but as the γ-sugar transiently produced may condense with preformed complexes, the products are often of greater complexity than methyldigalactoside (*loc. cit.*). Galactose and dextrose yield respectively a methyltetragalactoside and a methyltetraglucoside, $C_{25}H_{44}O_{21}$, whilst maltose gave a methyltrimaltoside, $C_{37}H_{64}O_{31},H_2O$. Towards Fehling's solution, the products behave as glucosides, whilst they also show the characteristic reactions of γ-compounds.

For experimental details, reference should be made to the original.   D. F. T.

The Degradation of Starch by Formaldehyde. H. MAGGI and G. WOKER (*Ber.*, 1918, **51**, 790—793. Compare A., 1917, i, 447, 686).—It has been shown that the dialysate obtained from a mixture of starch and formaldehyde has the properties of a solution of dextrin and simpler carbohydrates. A precipitate produced by adding alcohol to such a dialysate, redissolved in water, and allowed to become mouldy during the summer vacation, developed dextrose, identified as its osazone. Since the same mould produced dextrose from genuine dextrin, it is obvious that dextrin was present in the original dialysate, and since formic acid has no action on starch under the same conditions, the hydrolysis must be ascribed to the formaldehyde.   J. C. W.

Cellulose and Starch. JEAN SARASIN (*Arch. Sci. phys. nat.*, 1918, [iv], **46**, 5—32).—An inquiry into the constitution of cellulose and starch. A careful examination of the products of decomposition by heat of cellulose and starch indicates that in both cases l-glucosan is an intermediate product in the breaking-down process, and that this material itself when distilled under reduced pressure gives the same products as do starch and cellulose, in addition to the l-glucosan which they yield. Starch and cellulose are thus polymerides of l-glucosan, to which the author assigns the constitution (annexed formula), and he considers that it is the ring 2 which opens, giving two free valencies for the polymerisation, since amongst the products of decomposition of starch and cellulose 2:5-dimethylfuran is found.   W. G.

HO·HC——CH·OH
  | ¹ |
HC--O--CH
  | ² |
H₂C--O--CH·OH

Lignin. I. Lignosulphonic Acids. M. HÖNIG and JACQUES SPITZER (*Monatsh.*, 1918, **39**, 1—14. Compare Klason, A., 1908, i, 717).—The lignosulphonic acid obtained from different sulphite liquors varies considerably in composition (compare Seidel, *Mitt. k.k. Tech. Gewerbemuseums Wien.*, 1897, **7**, 287) and consists of a mixture of substances. By fractional precipitation of the calcium or barium salts from aqueous solution by alcohol, it is possible to obtain fractions of distinct composition approximating, for the barium salts, to the formulæ $C_{43}H_{50}O_{18}S_2Ba$, $C_{40}H_{44}O_{18}S_2Ba$, and $C_{74}H_{114}O_{48}S_2Ba$.   D. F. T.

A New Kind of Isomerism with Cobalt Compounds. Compounds containing Asymmetric Cobalt and Carbon. A. WERNER (*Helvetica Chim. Acta*, 1918, **1**, 5—32).—Among the three types of optically active cobaltammines which have been pre-

pared by Werner and his co-workers is the type represented by the *cis*-compound, [XCo en$_2$]X. If, now, one of the ethylenediamine groups is replaced by an unsymmetrical group, as, for example,

$$H_2N \cdot CH_2 \cdot CHR \cdot NH_2,$$

in place of the configuration (annexed formula), two structural formulæ can be written, since the unsymmetrical molecule can take up two different positions, namely,
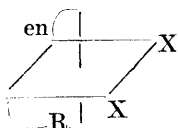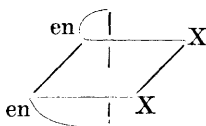
and
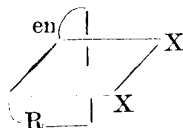
In the first formula the radicle R is far removed from the plane in which the two X-groups lie, whereas in the second formula it lies close to that plane. It follows that the *cis*-compound

$$\left[X_2Co \begin{array}{c} en \\ A \\ B \end{array} \right] X,$$ where AB represents an unsymmetrical group,
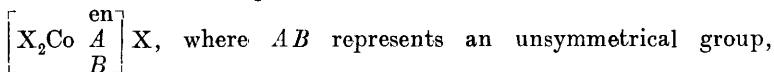
should give two series of salts. If, for example, AB is propylene-diamine (pn), there should be two series of *flavo*-salts, and this has actually been found to be the case. The two series are called the α- and β-series, the former giving salts which crystallise in prisms and the latter salts which crystallise in needles.

If, now, optically active propylenediamine is used, as well as optically active cobalt salt, further possibilities of the formation of isomerides occur. These possibilities, all of which have been realised experimentally, may be summarised as follows.

Eight optically active *flavo*-salts are possible, namely,

α- or prismatic series
{ *d*-propylenediamine { *d*-cobalt / *l*-cobalt
l-propylenediamine { *d*-cobalt / *l*-cobalt

β- or needle series
{ *d*-propylenediamine { *d*-cobalt / *l*-cobalt
l-propylenediamine { *d*-cobalt / *l*-cobalt
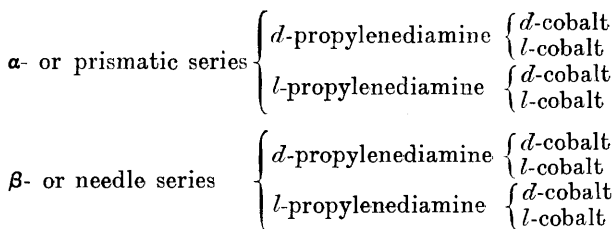
These optically active compounds can combine in different ways to give partly racemic compounds, which have also been prepared, namely:

(1) Four compounds which are racemic with respect to cobalt.

α- or prismatic series { *d*-pn-*d*-Co + *d*-pn-*l*-Co / *l*-pn-*d*-Co + *l*-pn-*l*-Co

β- or needle series { *d*-pn-*d*-Co + *d*-pn-*l*-Co / *l*-pn-*d*-Co + *l*-pn-*l*-Co
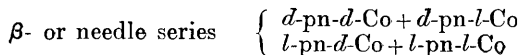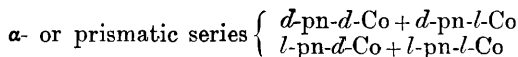
(2) Four compounds which are racemic with respect to propylene-diamine.

$$\alpha\text{- or prismatic series} \begin{cases} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn} \end{cases}$$

$$\beta\text{- or needle series} \begin{cases} d\text{-Co-}d\text{-pn} + d\text{-Co-}l\text{-pn} \\ l\text{-Co-}d\text{-pn} + l\text{-Co-}l\text{-pn} \end{cases}$$

Further, by combination of the α-salts of (1) and (2), and of the β-salts of (1) and (2), two completely racemic, and therefore inactive, compounds can be obtained.

Also, using optically active propylenediamine, the *trans*-isomeride (*croceo*-salt) of the formula $\left[X_2Co\dfrac{en}{pn} \right] X$ will give rise to three isomerides, namely :

$$\begin{matrix} d\text{-}trans\text{-compound} \\ l\text{-}trans\text{-compound} \end{matrix} \Big\} \, r\text{-}trans\text{-compound}.$$

The compound used as the starting point in this investigation was *dinitroethylenediaminepropylenediaminecobaltic nitrite*,

$$\left[(NO_2)_2Co\frac{en}{pn} \right] NO_2.$$
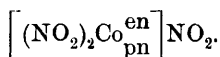
To obtain this, trinitrotriamminecobalt, $(NO_2)_3Co(NH_3)_3$, was prepared by heating Erdmann's salt, $[(NH_3)_2Co(NO_2)_4]K$, with the molecular-equivalent quantity of ammonium nitrate. By the action of ethylenediamine in aqueous solution, the following reaction is made to take place :

$$(NO_2)_3Co(NH_3)_3 + en = \left[(NO_2)_3Co\frac{NH_3}{en} \right] + 2NH_3,$$
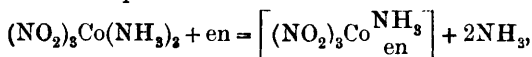
giving trinitroammine-ethylenediaminecobalt. When this is further treated with the molecular equivalent of active propylenediamine, the following reaction occurs :

$$\left[(NO_2)_3Co\frac{NH_3}{en} \right] + pn = \left[(NO_2)_2Co\frac{en}{pn} \right] NO_2 + NH_3,$$
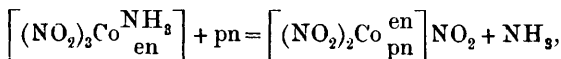
both *flavo*- and *croceo*-salts of dinitroethylenediaminepropylene-diaminecobaltic nitrite being produced. By adding alcohol to the reaction mixture (in solution), the *flavo*-salts are precipitated, whilst the *croceo*-salts remain in solution and can be obtained by concentration. By heating the crude *flavo*-nitrites with water and sodium bromide the bromides can be obtained, and then transformed into the *d*-bromocamphorsulphonates, which are then resolved and separated by fractional crystallisation. From the pure, active bromocamphorsulphonates the active bromides can be obtained by treatment with hydrobromic acid. The fractional crystallisations involved are long and tedious, and for details the original paper must be consulted.

Resolution of the *flavo-d*-pn-salts gave rise to four pure *bromo-camphorsulphonates*, which may be called *A*, *B*, *C*, and *D*. The

*t**

salts A and B belong to the prismatic series, and are optical anti-podes with respect to cobalt, as was shown by a study of their bromides. They have respectively $[\alpha]_D +10°$, $[\alpha]_E +100°$, and $[\alpha]_D +60°$, $[\alpha]_E +30°$. The salts C and D belong to the needle series, and are also optical antipodes with respect to cobalt; their specific rotations are respectively $[\alpha]_D +20°$, $[\alpha]_E +120°$, and $[\alpha]_D +0°$, $[\alpha]_E +140°$.

Similarly, resolution of the *flavo-l*-pn-salts gave four pure *bromo-camphorsulphonates*, A, B, C, and D. The prismatic salts A and B had $[\alpha]_D +106°$, $[\alpha]_E +10°$, and $[\alpha]_D +62°$, $[\alpha]_E +80°$ respectively. The needle salts C and D had $[\alpha]_D +70°$, $[\alpha]_E +92°$, and $[\alpha]_D +130°$, $[\alpha]_E +14°$ respectively. The pairs A and B and C and D were again optical antipodes with respect to cobalt.

The *flavo-dinitroethylenediaminepropylenediaminecobaltic brom-ides*, XBr, where $X = \left[(NO_2)_2 Co \begin{matrix} en \\ pn \end{matrix} \right]$, prepared from the above bromocamphorsulphonates, were all yellowish-brown in colour, A and B crystallising in prisms and C and D in needles. The specific rotations, $[\alpha]_D$, for the *d*-pn-series were:

	d-Co.	*l*-Co.
Prisms	$-30°$ (B)	$-60°$ (A)
Needles	$-6°$ (C)	$-108°$ (D)

The corresponding specific rotations for the *l*-pn-series were:

	l-Co.	*d*-Co.
Prisms	$+30°$ (B)	$+60°$ (A)
Needles	$+6°$ (C)	$+108°$ (D)

The *flavo-thiocyanates*, XCNS, were prepared from the bromides by treatment with sodium thiocyanate, and are yellow in colour. The specific rotations, $[\alpha]_D$, of the *d*-pn-series were: A, $-64°$, B, $-32°$, C, $-6·5°$, D, $-109°$, and of the *l*-pn-series: A, $+64°$, B, $+32°$, C, $+6·5°$, D, $+109°$.

The *flavo-sulphates*, X_2SO_4 (the isomeride A crystallises with $1H_2O$), were obtained from the bromides by reaction with ammonium sulphate. The specific rotations, $[\alpha]_D$, of the *d*-pn-series were: A, $-63°$. B, $-32°$, C, $-7°$, D, $-112°$, and of the *l*-pn-series, A, $+63°$, B, $+32°$, C, $+7°$, D, $+112°$.

The *partly racemic* flavo-*bromides*, XBr, were prepared synthetic-ally by combining the proper constituents in pairs. The follow-ing compounds containing racemic cobalt and active propylene-diamine were obtained. d-*pn-Series*: $A + B$, $[\alpha]_D -45°$; $C + D$, $[\alpha]_D -57°$. l-*pn-Series*: $A + B$, $[\alpha]_D +45°$; $C + D$, $[\alpha]_D +57°$. The compounds containing racemic propylenediamine and active cobalt were as follows: *d*-pn-$A + l$-pn-B, $[\alpha]_D -15°$; *d*-pn-$B + l$-pn-A, $[\alpha]_D +15°$; *d*-pn-$C + l$-pn-D, $[\alpha]_D +51°$; *d*-pn-$D + l$-pn-C, $[\alpha]_D -51°$.

All the above *flavo*-salts show strong optical dispersion, and curves are given showing their rotations for fifteen wave-lengths between $\mu\mu = 643·25$ and 492.

The completely *racemic* flavo-*salts* were prepared synthetically from the proper components, and were found to be inactive.

The croceo-*chlorides*, XCl, were prepared from the crude nitrites by treatment with cooled hydrochloric acid. They are golden-yellow in colour and less soluble than the bromides and iodides. The *d*-pn-chloride has $[a]_D -11°$ and the *l*-pn-chloride $[a]_D +12°$.

The d-*pn*- and l-*pn*-croceo-*nitrites*, XNO_2, have $[a]_D \mp 22°$, and the corresponding croceo-*bromides* $[a]_D \mp 10°$.   T. S. P.

Constitution of Internally Complex Metallic Salts. A. WERNER and SOPH. MATISSEN (*Helvetica Chim. Acta*, 1918, **1**, 78—84).—Tschugaev has already shown that when dioximes are introduced into metal-ammonias, the dioximino-radicle occupies two co-ordination positions. In order to see if this holds in other cases, the authors have introduced acetylacetone and benzhydroxamic acid, which readily give internally complex salts, into cobalt-ammonias, and have found that these also occupy two co-ordination positions. The action of acetylacetone and benzhydroxamic acid respectively on hydroxoaquodiethylenediaminecobalt salts gives rise to acetylacetonato- and benzhydroxamato-diethylene-diaminecobalt salts, which have the following general formulæ:
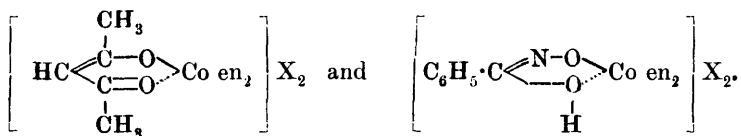
Acetylacetonatodiethylenediaminecobalt bromide, YBr_2,H_2O, where $Y = [C_5H_7O_2Co\,en_2]$, is prepared by heating a solution of 1 gram of hydroxoaquodiethylenediaminecobalt bromide in 10 c.c. of water with 0·6 gram of acetylacetone on the water-bath under reflux for half an hour, and then concentrating to half its volume. The bromide is precipitated by the addition of sodium or potassium bromide, and forms large, garnet-red crystals. By appropriate double decomposition of the bromide with other salts, as, for example, with potassium iodide to give the iodide, or with silver chloride to give the chloride, the following salts were prepared. The *iodide*, YI_2,H_2O, forms garnet-red prisms; the *chloride*, $YCl_2,2H_2O$, gives dark red crystals; the *nitrate*, $Y(NO_3)_2$, crystallises in large, well-developed garnet-red crystals; the *sulphate*, $YSO_4,2H_2O$, forms long, red needles; and the *perchlorate*, $Y(ClO_4)_2$, crystallises in large, ruby-red columns.

Benzhydroxamatodiethylenediaminecobalt bromide, YBr_2, where $Y = [C_7H_6O_2NCo\,en_2]$, is prepared by heating a solution of 1 gram of hydroxoaquodiethylenediaminecobalt bromide in 10 c.c. of water with the molecular-equivalent quantity of benzhydroxamic acid under reflux for half an hour. The solution is filtered from a light-coloured by-product and the bromide precipitated by the addition of sodium or potassium bromide. It forms large, almost black crystals with a metallic glance. The following salts were prepared from the bromide by methods similar to those mentioned for the acetylacetonato-salts. The *perchlorate*, $Y(ClO_4)_2$, forms large,

t 2

violet crystals possessing a metallic glance; the *dithionate*, $YS_2O_6,2H_2O$, crystallises in fine needles; the *thiocyanate*, $Y(SCN)_2$, gives dark violet, metallic-glistening octahedra; and the *sulphate*, $YSO_4,3H_2O$, crystallises in rose-coloured, long, hair-like needles.

<div align="right">T. S. P.</div>

The Constitution of Carbamides. VI. Mechanism of the Synthesis of Urea from Urethane. EMIL ALPHONSE WERNER (T., 1918, **113**, 622—627).—Although the vapour density of urethane at 203° approximates to the theoretical, the ester gradually decomposes when boiled under reflux, yielding ethyl alcohol and cyanic acid, the latter being found as cyanuric acid. The formation of urea from ammonia and urethane is therefore not a simple case of the conversion of an ester into an amide, but is actually a modification of Wöhler's synthesis, involving the union of ammonia and cyanic acid. Similarly, the decomposition of urethane by aqueous alkali is not a direct hydrolysis, as is commonly assumed, but actually occurs by the stages $OEt \cdot CO \cdot NH_2 \longrightarrow OEt \cdot C(ONa):NH \longrightarrow EtOH + NaOCN \longrightarrow NaHCO_3 + NH_3$. On the other hand, when heated in a current of hydrogen chloride, urethane gives carbon dioxide, ethyl chloride, and alcohol, the acid therefore appearing to favour the constitution $OEt \cdot CO \cdot NH_2$, whereas alkali favours the constitution $OEt \cdot C(OH):NH$. When urethane is heated in aqueous solution at 130°, it gives rise to urea without the independent addition of ammonia, the cyanic acid arising from the dissociation of the urethane undergoing hydrolysis to urea. The relative difficulty of formation of urea from ethyl carbonate or carbamate and ammonia supports the view that urea does not contain two amino-groups, and the suggestion is made that two amino-groups, like two hydroxyl groups, cannot be attached stably to one carbon atom.

For experimental details, reference should be made to the original.

<div align="right">D. F. T.</div>

The Constitution of Dicyanodiamide. WILLIAM J. HALE and FRANK C. VIBRANS (*J. Amer. Chem. Soc.*, 1918, **40**, 1046—1063).—Of the many constitutions which have been proposed for dicyanodiamide, the authors' experiments favour the cyanoguanidine structure, $NH_2 \cdot C(:NH) \cdot NH \cdot CN$, suggested by Bamberger in 1880. Pohl (A., 1908, i, 575) found that about one-half of the total nitrogen in the molecule is eliminated by sodium hypobromite, and, assuming that only an amino-group can react to this end, proposed the constitution $C(NH_2)_2:N \cdot CN$. The authors, however, using 20% sodium hypochlorite, have eliminated three-fourths of the nitrogen, the remaining atom being that in the cyano-group.

The quantity of nitrogen liberated by the reaction between dicyanodiamide and nitrous acid depends on the temperature and the concentration of the acid used as solvent. With 50% acetic acid as solvent, no nitrogen was evolved at the ordinary temperature, and at the b. p. only an amount corresponding with one-

quarter of an atom. With 85% acetic acid at the b. p. one atom of nitrogen was eliminated, with 95% acid two atoms, with glacial acetic acid about three atoms, whilst with 85% phosphoric acid all the nitrogen in dicyanodiamide was eliminated in the elementary state. Dicyanodiamide, therefore, undoubtedly contains one amino-group, as is evidenced by the comparative ease with which the first atomic proportion of nitrogen is eliminated. If a second amino-group were present, its interaction with nitrous acid should proceed under practically the same conditions. The development of a second amino-group in the course of the decomposition might therefore account for the higher temperature and longer time necessary for interaction with a second molecule of nitrous acid. The authors have failed to find a compound containing an amino-group which in 85% acetic acid at the b. p. does not react with nitrous acid; even guanidine, which, as stated by Van Slyke, fails to yield any nitrogen in 50% acetic acid at the ordinary temperature, yields two atomic proportions (but never more than two) in hot, more concentrated acetic acids. The fact that the condensation product of dicyanodiamide and formaldehyde, to which Pohl (*loc. cit.*) ascribes the constitution $OH \cdot CH_2 \cdot NH \cdot C(NH_2){:}N \cdot CN$ derived from his formula for dicyanodiamide, does not yield any nitrogen in 85% acetic acid suffices, therefore, to disprove Pohl's constitution, leaving for the condensation product the alternative constitution $OH \cdot CH_2 \cdot NH \cdot C({:}NH) \cdot NH \cdot CN$ derived from the Bamberger formula for dicyanodiamide.

When an aqueous solution of dicyanodiamide and acetylacetone is boiled with a little 2N-sodium hydroxide, a substance, $C_7H_8N_4$, is obtained which does not contain a primary amino-group, but responds to the Liebermann and the Hinsberg tests for secondary amines. The formation of this substance disproves, according to the authors, Pohl's formula for dicyanodiamide, since they assert that this would lead to the formula of a condensation product containing neither primary nor secondary amino-groups. The substance $C_7H_8N_4$ is regarded as 2-*imino*-1-*cyano*-4 : 6-*dimethyl*-1 : 2-*dihydro-pyrimidine*, $NH{:}C{<}^{N{=\!=\!=}CMe}_{N(CN) \cdot CMe}{>}CH$. It forms colourless needles, m. p. 225°, yields a *silver* salt, $C_7H_7N_4Ag$, and is converted by boiling dilute sulphuric acid (1 : 5) into 2-*imino*-4 : 6-*dimethyl*-1 : 2-*dihydropyrimidine*, $C_6H_9N_3,H_2O$, lemon-yellow prisms, m. p. 199° (decomp.; anhydrous), which yields the well-known acetyl-acetonecarbamide when boiled with 4N-sodium hydroxide.

The condensation of dicyanodiamide (Bamberger's formula) and acetylacetone could yield a product which might be 2-imino-1-cyano-4 : 6-dimethyl-1 : 2-dihydropyrimidine (as stated above) or 2-cyanoamino-4 : 6-dimethylpyrimidine, but the latter alternative is excluded, because the product does not give Combes's aminodi-methylpyrimidine on hydrolysis with boiling dilute sulphuric acid.

C. S.

Mercury Fulminate. W. R. HODGKINSON (*J. Soc. Chem. Ind.*, 1918, **37**, 190T).—The author points out that mercury fulminate

cannot be formed in the absence of nitrous acid or a mixture of nitric oxide and nitrogen peroxide; he therefore represents the formation and constitution of fulminic acid by the equation:

$$\begin{matrix} CH_3 \\ | \\ OH \cdot CH_2 \end{matrix} + \begin{matrix} O\text{:}N \\ O\text{:}N \end{matrix}\!\!>\!\!O \;=\; \begin{matrix} CH\text{:}N \\ | \\ OH \cdot C\!\!=\!\!N \end{matrix}\!\!>\!\!O + 2H_2O.$$

<div align="right">J. F. S.</div>
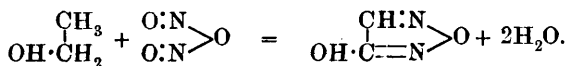
The Decomposition of Solutions of Hydrocyanic Acid.

W. Lewcock (*Pharm. J.*, 1918, **101**, 50—51).—The decomposition of solutions of hydrocyanic acid with the formation of a yellow or brown coloration or deposit is attributed to the action of small quantities of basic substances which are principally derived from the glass vessels, but might also be introduced by the use of hard water in preparing the solutions. A similar decomposition is observed in concentrated solutions of sodium cyanide on the addition of sodium carbonate, but not in presence of sodium hydroxide. In this case, it would appear that the alkali influences the hydrogen cyanide liberated by hydrolysis of the cyanide, whereas in presence of sodium hydroxide this hydrolysis is suppressed. Experiments showed that the addition of bases and salts with alkaline reaction greatly accelerated the decomposition of dilute solutions of hydrocyanic acid. The effect of bases derived from glass was studied by sealing up portions of an 8% solution of hydrocyanic acid with finely powdered glass, together with various substances which might be expected to retard the decomposition, and observing the length of time required for the appearance of a yellow coloration. The retardation was most marked in the presence of acids, and the addition of 1% of sulphuric acid, calculated on the weight of hydrocyanic acid, delayed the appearance of the colour for twenty-three days, as compared with two days in the case of the solution of hydrocyanic acid in distilled water. Tartaric acid equivalent to half the above quantity of sulphuric acid preserved the solution for twelve days, and saturation with carbon dioxide delayed decomposition for thirteen days. The preservative effect of various substances in the presence of glass would therefore appear to depend essentially on their acidity, and it was found that substances such as alcohol, glycerol, and mannitol were entirely without influence. With a higher concentration of tartaric acid (0·04 gram in 5 c.c.), the 8% solution of hydrocyanic acid remained unaffected in the presence of glass for more than four months, and it is concluded that 10% of sulphuric acid, on the weight of the hydrocyanic acid, would preserve the solution indefinitely.   J. F. B.

Complex Uranyl Compounds.

Arno Müller (*Zeitsch. anorg. Chem.*, 1918, **103**, 55—68).—A number of complex compounds of the uranyl radicle with cacodylic acid, *o*-, *m*-, and *p*-sulphaminobenzoic acids, toluene-*o*-sulphonic acid, and α-phenylcinchonic acid have been prepared. The cacodylic acid compound

is of special interest on account of its therapeutic properties. By treatment with hydrogen sulphide in alcoholic suspension, it is converted into a dithio-derivative.

Uranyl cacodylate, $UO_2[AsO_2(CH_3)_2]_2$, is prepared by double decomposition of sodium cacodylate and uranyl acetate. It forms a bright yellow, odourless, and tasteless powder, is decomposed by acids and alkalis, and when strongly heated evolves cacodyl vapours, leaving a residue of U_3O_8.

Uranyl thiocacodylate, $UO_2[AsOS(CH_3)_2]_2$, is difficult to isolate owing to its instability. By evaporating its alcoholic solution in a vacuum desiccator, it is obtained as a reddish-brown, crystalline mass with a mercaptan-like odour, m. p. 60—65°.

Uranyl o-sulphaminobenzoate, $UO_2[C_6H_4(SO_2 \cdot NH_2) \cdot CO_2]_2,3H_2O$, forms small, greenish-yellow crystals with a metallic taste. *Uranyl m-sulphaminobenzoate* forms a dihydrate. *Uranyl p-sulphaminobenzoate* forms a monohydrate.

Uranyl toluene-o-sulphonate, $UO_2[C_7H_7 \cdot SO_3]_2,2H_2O$, forms fairly large, bright yellow leaflets.

Uranyl α-phenylcinchonate, $UO_2[C_9NH_5Ph \cdot CO_2]_2$, is a dark yellow, tasteless and odourless amorphous powder.   E. H. R.

Dissociation as a General Phenomenon with Hydrocarbons. HANS MEYER and ALICE HOFMANN (*Monatsh.*, 1918, **39**, 107—128).—The observed action of heat on organic substances, particularly hydrocarbons, indicates the occurrence of dissociation of hydrogen from carbon at a C–H-linking; the effect is not appreciable at the ordinary temperature, but becomes so when the dissociation process is favoured by rise of temperature, the influence of light, and of electrical or radioactive radiation. Substances which will remove one or other of the products of the dissociation should also extend its effect, and examples are quoted in which oxidation is already known to cause a condensation of two aromatic nuclei. The general evidence supplied by the nature of the constituents of coal tar supports the further view that in pyrogenic reactions long side-chains tend to become shortened, and this accords well with the fact that longer chains are more easily attacked, for example, by oxidising agents.

An examination of anthracene oil revealed the presence of diphenyl, together with a mixture of the ditolyls, but dibenzyl could not be detected. *iso*Propylbenzene when heated strongly decomposes mainly into toluene and trioxymethylene, the latter arising from the severed methylene groups. Methyl phthalate gives methyl benzoate, formaldehyde, and methyl diphenyltricarboxylate. Methyl acetate gives α-trioxymethylene as the main product, and no ethyl succinate. The action of sunlight on a suspension of ethyl dihydrolutidinedicarboxylate in benzene gives ethyl lutidinedicarboxylate.   D. F. T.

Nomenclature of Singly- and Multiply-divided Carbon Rings. Bridge Linking. J. BREDT and MARIA SAVELSBERG (*J. pr. Chem.*, 1918, [ii], **97**, 1—22).—After reviewing the various

methods of nomenclature suggested hitherto for cyclic organic compounds containing bridged linkings and indicating their respective weaknesses, the authors suggest a scheme in which as far as possible the numbering of the carbon atoms is commenced at an atom possessing no symmetrical counterpart in the molecule, and, in the numbering, careful consideration is given to planes of symmetry in the molecule. The conception of a "bridge" is limited by the exclusion of molecules in which the bridge exists between two ortho-positions in a *cyclo*hexane ring, such compounds, for example, decahydronaphthalene, being classified as containing condensed nuclei. With more complex cyclic molecules, the excesive use of numbers is avoided as far as possible by the use of names, so that each number represents a single position. The various cyclic systems as far as possible are referred to *cyclo*hexane, and are grouped into (*a*) single rings, (*b*) double rings containing a meta- or para-bridge, or composed of rings condensed together by an amphi- or a spiro-attachment, and polycyclic compounds containing bridges together with a peri-linking, or consisting of combinations of (*a*) and (*b*).

The following examples illustrate this system of nomenclature. In the camphane and fenchane group, the molecule of camphor (annexed formula, I) may be taken as typical, the corresponding name being *p-meso*methylene-1 : 1 : 2ᵃ-trimethyl*cyclo*hexan-3ᵃ-one. The atoms in compounds of the pinane group are distinguished by

$$\begin{array}{ccc}
\overset{3^{\beta'}}{C}H_2 - \overset{2^\beta}{C}H - \overset{3^\beta}{C}H_2 \\
| \qquad \overset{1}{C}Me_2 \qquad | \\
\overset{3^{a'}}{C}H_2 - \overset{2^a}{C}Me - \overset{3^a}{C}O
\end{array}$$

(I.)

$$\begin{array}{ccc}
\overset{3^\beta}{C}H - - - \overset{2^\beta}{C}Me \\
CH_2 \cdot CMe_2 \quad CH \; 1 \\
\overset{3^a}{C}H - - - \overset{2^a}{C}H_2
\end{array}$$

(II.)
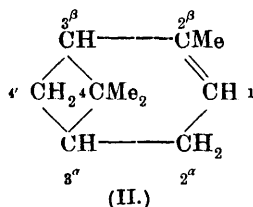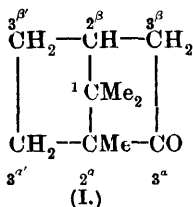
the method shown in formula II (annexed), which shows pinene to be *m-meso*methylene-4 : 4 : 2β-trimethyl*cyclo*-Δ¹, ²β-hexene. By the idea of a bridged ring as defined above, the carane group is excluded from the new system of nomenclature; its inclusion offers no great difficulty, but preference is given to the description of carane as *amphi*methylene*cyclo*hexane. The carbon atoms in tricyclene

$$\begin{array}{ccc}
\overset{3^{\beta'}}{C}H_2 - \overset{2^\beta}{C}H - - - \overset{3^\beta}{C}H_2 \\
| \quad \overset{1}{C}Me_2 \quad | \\
\overset{3^{a'}}{C}H - - - \overset{3^a}{C}H \\
\overset{2^a}{C}Me
\end{array}$$

(III.)
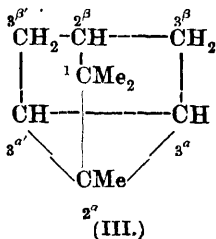
(*a-pericyclo*camphane) are numbered as in formula III (annexed), the corresponding name being *p-meso*methylene-1 : 1 : 2ᵃ-trimethyl-3ᵃᵃ'-*pericyclocyclo*hexane, whilst as further examples may be mentioned Buchner's condensation product of ethyl diazoacetate and bornylene, which receives the name ethyl *p-meso*methylene-1 : 1 : 2-trimethyl*cyclo*hexane-*amphi*-3ᵃβ-methylenecarboxylate (formula IV), and the parent hydrocarbon of Forster's hydroxy-

camphene (formula V), which is described as *p-meso*methylene-1 : 1-dimethyl*cyclo*hexane-*amphi*-2ᵃ : 3ᵃ-methylene.

$$
\begin{array}{ll}
\overset{3^{\beta'}}{C}H_2 - \overset{2^{\beta}}{C}H - \overset{3^{\beta}}{C}H & \\
\quad | \quad {}_1CMe_2 \quad |\!\!>\!CH \cdot CO_2Et & \\
CH_2 - CMe - CH & \\
{}_{3^{\alpha'}} \quad {}_{2^{\alpha_i}} \, : \quad {}_{3^{\alpha}} &
\end{array}
\qquad
\begin{array}{ll}
CH_2 - CH - CH_2 & \\
| \quad {}_1CMe_2 \quad | & \\
CH_2 - C - CH_2 & \\
{}_{2^{\alpha}} \quad | \quad {}_{3^{\alpha}} & \\
\quad\quad CH_2 &
\end{array}
$$

(IV.)   (V.)
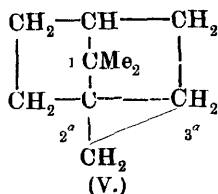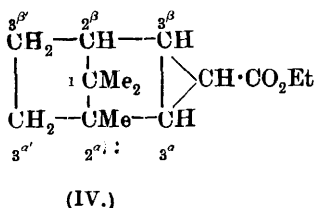
                                     D. F T.

Nitrosotriphenylamine and Colours of the Second Order.

Jean Piccard and Morris Kharasch [and, in part, E. H. Fleck] (*J. Amer. Chem. Soc.*, 1918, **40**, 1074—1079).—It is well known that the colour of a yellow dye is lowered by increase of molecular weight through orange, red, violet, blue, to green owing to a shift of its maximum absorption band towards the red end of the spectrum. Absorption colours have much in common with interference colours, and the first absorption band or group of bands is always followed by a second one, which is the octave of the first. When a dye with a lower colour than green is prepared, therefore, colours of the second order are obtained (Piccard, A., 1913, i, 895), but hitherto dyes giving more than a yellowish-green or greenish-yellow have not been prepared. The authors have now prepared an orange compound of the second order. A suspension of triphenylamine (prepared by heating diphenylamine and iodobenzene in nitrobenzene with an excess of potassium carbonate and a little catalytic copper at 207° for twelve hours) in absolute alcohol saturated with hydrogen chloride was slowly treated at −5° with amyl nitrite, dry hydrogen chloride being passed through the mixture. The crude, orange-red or carmine hydrochloride is suspended in cold water for two hours, the resulting crude base is collected, washed with cold water, dried in a vacuum desiccator, dissolved in dry ether, and the solution treated with hydrogen chloride, whereby p-*nitrosotriphenylamine hydrochloride* (*diphenylbenzoquinonemonoimine oxime chloride*), $OH \cdot N : C_6H_4 : NPh_2Cl$, is obtained; it crystallises in long, brown needles, m. p. 178°. p-*Nitrosotriphenylamine*, $NO \cdot C_6H_4 \cdot NPh_2$, obtained by hydrolysing the preceding hydrochloride with water, forms long, brown needles (orange when powdered), m. p. 120·5° (corr.), gives a yellow solution in benzene and an orange solution in alcohol, and yields Herz's p-acetylamino-triphenylamine by reduction with zinc and acetic acid, followed by acetylation. The colours of the base and its hydrochloride are alike, but that of the former is orange of the second order and that of the hydrochloride orange of the first order.   C. S.

Sulphur β-Naphthyl Chlorides. [β-Chlorothiolnaphthalenes.]

Th. Zincke and K. Eismayer (*Ber.*, 1918, **51**, 751—767. Compare A., 1912, i, 762; 1915, i, 234).—When β-thiolnaphthalene

is treated with chlorine, it first suffers oxidation to the disulphide, then changes into the unstable β-chlorothiolnaphthalene, and finally yields 1-chloro-β-chlorothiolnaphthalene. This is a comparatively stable substance, capable of taking part in many reactions, a number of which are described.

β-Thiolnaphthalene is obtained by the reduction of crude naphthalene-β-sulphonyl chloride with zinc dust in alcoholic solution. β-Chlorothiolnaphthalene, prepared by the action of chlorine (1 mol.) in dry chloroform, is a yellowish-red powder, m. p. 50—60°, which readily changes into di-β-naphthyl disulphide on treatment with alkalis, alcohol, acetone, aniline, or β-naphthol, or when kept. 1-Chloro-β-chlorothiolnaphthalene, $C_{10}H_6Cl\cdot SCl$, the product obtained by using twice the amount of chlorine, forms small, hard, yellowish-red crystals, m. p. 74—75°. This is oxidised by chlorine in glacial acetic acid solution to 1-chloronaphthalene-β-sulphonyl chloride, m. p. 84—85° (compare Cleve, A., 1892, 345), the corresponding anilide having m. p. 171—172°.

Methyl 1-chloro-β-naphthylsulphinite, $C_{10}H_6Cl\cdot S\cdot OMe$, an almost colourless, unstable oil, is prepared by the action of dry sodium methoxide on the chlorothiol, but the corresponding acid is unknown. Attempts to isolate it, for example, by the action of N-sodium carbonate on the chlorothiol, result in the formation of the anhydride, di-1-chloro-β-naphthyl sulphoxide [di-1-chloro-β-thionaphthyl oxide], $O(S\cdot C_{10}H_6Cl)_2$, which separates in pale yellow crystals, m. p. 149°. This is reconverted into the chlorothiol by means of phosphorus pentachloride, whilst warm N-sodium hydroxide transforms it into di-1-chloro-β-naphthyl disulphide, $S_2(C_{10}H_6Cl)_2$, thin, glistening leaflets, m. p. 141—142°, and 1-chloro-β-naphthylsulphinic acid, $C_{10}H_6Cl\cdot SO_2H$, felted needles, m. p. 138—139° (methyl ester, from the silver salt, long needles, m. p. 139—140°). If the oxide is boiled with glacial acetic acid, it changes into di-1-chloro-β-naphthyl disulphoxide,

$$C_{10}H_6Cl\cdot SO\cdot SO\cdot C_{10}H_6Cl ;$$
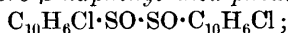
this may also be prepared by the interaction of the chlorothiol and the silver salt of the foregoing sulphinic acid, and it crystallises in colourless, prismatic needles, m. p. 152—153°, and liberates iodine from potassium iodide.

The chlorothiol reacts with bases in indifferent solvents to form "thiolamines" and "dithiolimines," $C_{10}H_6Cl\cdot S\cdot NR_2$ and

$$NR(S\cdot C_{10}H_6Cl)_2,$$
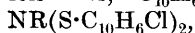
where R = H or a radicle. Thus, aqueous ammonia yields 1-chloro-β-naphthylthiolamine, which crystallises in small, stout needles, m. p. 160° (becomes red at 95° and partly decomposes at 105—110°), and forms a benzylidene compound, $C_{10}H_6Cl\cdot S\cdot N{:}CHPh$, m. p. 106—107°. Ethereal ammonia produces di-1-chloro-β-naphthyldithiolimine as a pale pink powder, m. p. 213—214°, which may also be obtained by treating the amine with glacial acetic acid in the cold. Methylamine yields 1-chloro-β-naphthylthiolmethylamine, small leaflets, m. p. 89—90°, and the imine, $NMe(S\cdot C_{10}H_6Cl)_2$, m. p. 177—178°. 1-Chloro-β-naphthylthiolanilide, prismatic

needles, m. p. 132°, -α-*naphthylidide*, hard crystals, m. p. 154°, and -β-*naphthylidide*, small needles, m. p. 132—133°, are prepared from the amines in benzene solution.

The naphthylamines behave differently if applied to the chlorothiol in warm glacial acetic acid solution. In these circumstances, the reaction resembles the coupling of a diazonium chloride with the bases. Thus, α-naphthylamine yields 2:4-*di*-1′-*chloro*-β-*naphthylthio*-α-*naphthylamine* [1-*aminonaphthyl* 2:4-*di*-1′-*chloro*-β-*naphthyl disulphide*], $NH_2 \cdot C_{10}H_5(S \cdot C_{10}H_6Cl)_2$, m. p. 85—87°, which forms an *acetyl* derivative, m. p. 144—145°, and a red azodye with β-naphthol, whilst β-naphthylamine gives 1-*chloro*-β-*naphthyl* 2-*amino*-α-*naphthyl sulphide*, in prisms and needles, m. p. 183—184°. The latter yields a *diacetyl* derivative, m. p. 153—154°, gives azo-dyes, and reacts with the original chlorothiol to form the *compound*, $C_{10}H_6Cl \cdot S \cdot NH \cdot C_{10}H_6 \cdot S \cdot C_{10}H_6Cl$, m. p. 187—188°.

The chlorothiol also resembles a diazonium chloride in its reactions with tertiary aromatic amines and phenols, except that the components usually need to be heated to ensure success. Dimethylaniline yields p-*dimethylaminophenyl* 1-*chloro*-β-*naphthyl sulphide*, $C_{10}H_6Cl \cdot S \cdot C_6H_4 \cdot NMe_2$, prisms and needles, m. p. 120—121°. α-Naphthol gives 1-*chloro*-β-*naphthyl* 4-*hydroxy*-α-*naphthyl sulphide*, $C_{10}H_6Cl \cdot S \cdot C_{10}H_6 \cdot OH$, m. p. 116—118° (*acetate*, m. p. 138—139°); β-naphthol forms 1-*chloro*-β-*naphthyl* 2-*hydroxy*-α-*naphthyl sulphide*, large needles, m. p. 142—143° (*acetate*, m. p. 123—124°); and resorcinol yields op-*dihydroxyphenyl* 1-*chloro*-β-*naphthyl sulphide*, glistening leaflets, m. p. 153—154° (*diacetate*, m. p. 83—84°).

The chlorothiol also reacts with a number of ketones. For example, acetone gives 1-*chloro*-β-*naphthyl acetonyl sulphide* (1-*chloro*-β-*naphthylthiomethyl methyl ketone*),

$$C_{10}H_6Cl \cdot S \cdot CH_2 \cdot COMe,$$
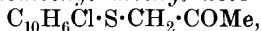
in colourless needles, m. p. 70—71°, which forms a *hydrazone*, glistening leaflets, m. p. 202°.

Potassium cyanide converts the chlorothiol into 1-*chloro*-β-*naphthyl thiocyanate*, $C_{10}H_6Cl \cdot SCN$, m. p. 118—119°.

J. C. W.

Preparation of a New Type of Organic Sulphur Compound. GERALD NOEL WHITE (T., 1918, **113**, 608—609).—When β-naphthyl disulphide is heated with sodium sulphide crystals and sulphur, it gradually dissolves in the sodium polysulphide solution first formed. On cooling, glistening lamellæ of *sodium* β-*naphthylthiosulphoxylate* separate, from which the free *acid*,

$$\begin{array}{c} C_6H_4 \cdot CH \\ CH{=}CH \end{array}\!\!\!>\!C \cdot S \cdot SH,$$

is liberated by dilute hydrochloric acid. The *lead* salt, obtained by double decomposition as an orange precipitate, on keeping gradually decomposes, the colour passing through scarlet to brown and black, whilst when heated with alcohol it yields β-naphthyl disulphide.

D. F. T.

The Hydrindene-1 : 2-diols.   J. BÖESEKEN and CHR. VAN LOON *(Proc. K. Akad. Wetensch. Amsterdam,* 1918, **20**, 1186—1191).— The authors have repeated the work of Heusler and Schieffer (compare A., 1899, i, 365), and consider that they had obtained an impure *cis*-1 : 2-dihydroxyhydrindene, which is now found to have m. p. 107·5—108°. The diol described by Weissgerber (A., 1911, i, 623) is not really pure, but when obtained in the pure state from indene dibromide it is the *trans*-1 : 2-dihydroxyhydrindene, m. p. 159·8—160° (corr.). It gives a *diacetate,* b. p. 169—169·5°/ 13 mm. (corr.), $D_4^{29\cdot4}$ 1·1771, n_D^{20} 1·5170. The *cis-dibenzoate* has m. p. 109·5—110·5° (corr.), and the trans-*dibenzoate,* m. p. 76·5—77·5° (corr.), whilst the corresponding *phenylurethanes* have m. p. 205° (decomp.; corr.) and 206·5° (decomp.; corr.) respectively. A polymorphic modification of the *cis*-diol, m. p. 100·5—101·5° (corr.), obtained during the hydrolysis of the *cis*-dibenzoate, is described.

Indene oxide, $\begin{matrix} CH_2-CH \\ C_6H_4\cdot CH \end{matrix}\!\!>\!O$, m. p. 31—31·5°, b. p. 113°/19·5 mm. (corr.), $D_4^{23\cdot6}$ 1·1258, $n_D^{23\cdot1}$ 1·5627, was obtained by the decomposition of bromohydroxyhydrindene by potassium hydroxide in ether. This oxide, as well as the *cis-* and *trans*-dihydroxyhydrindenes, readily gave β-hydrindone when warmed with dilute sulphuric acid. Indene oxide when carefully hydrated gave a mixture of the *cis-* and *trans*-glycols   W. G.

Synthesis of Derivatives of Phenylethyl Alcohol.   JOSE RANEDO *(Anal. Fis. Quim.,* 1918, **16**, 351—354).—Magnesium benzyl chloride and chloromethyl ethyl ether, $CH_2Cl\cdot OEt$, react to form *phenylethyl ethyl ether,* $CH_2Ph\cdot CH_2\cdot OEt$, a liquid, b. p. 193—196°. Oxidation with chromic acid converts this substance into benzoic acid, and phosphorus pentachloride yields a liquid which decomposes when distilled at ordinary pressure into hydrogen chloride and a liquid, b. p. 200°.   A. J. W.

Sitosterol.   A. WINDAUS and ERIK RAHLEN *(Zeitsch. physiol. Chem.,* 1918, **101**, 223—235).—In the presence of palladium, sitosterol in acetic acid solution is reduced by hydrogen at 100°, forming *sitostanol,* $C_{27}H_{48}O$, flat four- or six-sided plates from alcohol, m. p. 137°, $[α]_D^6 + 27\cdot9°$; *acetate,* m. p. 132°. The new compound closely resembles cholestanol, and on oxidation with chromic acid yields *sitostanone,* $C_{27}H_{46}O$, plates from alcohol, m. p. 157°, $[α]_D^4 + 45\cdot7°$, and, with excess of chromic acid, *sitostandicarboxylic acid,* $C_{27}H_{46}O_4$, plates from acetic acid, m. p. 225—227°. Both the latter compounds are analogous to, but not identical with, the corresponding cholesterol derivatives, cholestanol, and cholestandicarboxylic acid. On distillation of a mixture of sitostandicarboxylic acid and acetic anhydride at 280° in a vacuum, carbon dioxide and water are evolved, and a cyclic *ketone* produced, $C_{26}H_{44}O$, well-formed hexagonal crystals from methyl alcohol, m. p. 112°. Reduction of sitostanone with zinc amalgam in boiling acetic

acid solution yields the hydrocarbon, *sitostan*, $C_{27}H_{48}$, m. p. 85—85·5°, which resembles cholestan (m. p. 80—81°), but is certainly not identical with it. The observed differences between these derivatives of sitosterol and the corresponding ones derived from cholesterol indicate that the general resemblance of the parent substances cannot be ascribed to the possession of a common structure with a difference in the position of the hydroxyl radicle, the double linking, or of both. The difference between sitosterol and cholesterol must therefore be structural or steric.   H. W. B.

Anodic Formation of Ester simultaneously with Nitrobenzene and *o*-Nitrophenol from the Mononitrobenzoic Acids. C. SCHALL (*Zeitsch. Elektrochem.*, 1918, **24**, 154—157).—A mixture of potassium *o*-nitrobenzoate and the free acid in acetic anhydride solution has been subjected to electrolysis at the ordinary temperature. The anode products of the electrolysis were nitrobenzene, *o*-nitrophenol, and the *o*-nitrophenyl ester of *o*-nitrobenzoic acid. The yield of the products depends on the temperature. In concentrated aqueous solutions of potassium acetate and *o*-nitrobenzoate, the anode products are nitrobenzene, *o*-nitrophenol, and methyl *o*-nitrobenzoate. The formation of the nitrophenol is to be regarded as an anodic oxidation product, since this substance is produced by the action of persulphate on the *o*-nitrobenzoate. The formation of nitrobenzene, which is the analogue of methane in the acetate electrolysis, is stated to be due to the thermal decomposition of an intermediate compound of a peroxide nature.   J. F. S.

The Direct Conversion of Nitriles into Esters. PAUL PFEIFFER (*Ber.*, 1918, **51**, 805).—With reference to Spiegel's communication (this vol., i, 216), the author points out that examples of the direct conversion of nitriles into esters were given in his work on stilbene-*o*-carboxylic acids some years ago (A., 1911, i, 448), where he also directed attention to the steric hindrance of a methyl group in the ortho-position.   J. C. W.

Direct Preparation of Aromatic Nitriles by Catalysis. ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], **23**, 235—238).— Aromatic nitriles may be readily prepared with good yield by passing the vapours of the esters of the corresponding acids along with ammonia over aluminium or thorium oxides at 470—480°. This method has been successfully used with the methyl, ethyl, propyl, or *iso*amyl esters of benzoic, the three toluic, phenylacetic, and α- and β-naphthoic acids.   W. G.

The Nature of Subsidiary Valencies. XVIII. Octammines. Influence of the Volume of the Anion. FRITZ EPHRAIM [with E. ROSENBERG] (*Ber.*, 1918, **51**, 644—669. Compare this vol., ii, 115).—In the course of this work it has often been demonstrated that the ability of a substance to form additive compounds is intimately connected with the magnitude of the space

occupied by the various parts of the molecule. It is now shown that when the anion is particularly large, the additive capacity of the cation for negative substances becomes much more than it is normally. For example, very few cases of metallic ammines are known in which the number of molecules of ammonia is more than six, but several are now described, being salts of bivalent metals with aromatic acids, in which the number is eight. In explaining this, the author offers a picture of the arrangement of the metallic atoms within the crystal, each one surrounded by eight acid radicles; the larger these radicles are, the more room will there be for ammonia molecules around the metallic atom. He refers, in this connexion, to the remarkable fact that polyhydrates of some salts can combine with several molecules of hexameth lene-tetramine, and, conversely, compounds of salts with hexamethylenetetramine or caffeine can combine with more water molecules than the salts alone (see A., 1911, i, 184, 266; 1912, i, 812).

That the chemical nature of the anion is not the factor which confers this extra additive capacity on the salt is proved by the fact that the corresponding alkali salts have no affinity for ammonia, and that carboxylates and sulphonates alike give rise to octammines. Additional evidence that the controlling factor is a spatial one is adduced from the fact that salts of dibasic acids, like phthalic and naphthalic acids, do not form octammines, whereas benzoates do.

Even in the aromatic series, however, the experimental material is by no means plentiful, for it so frequently happens that internal complexes are formed between some substituent in the acid and the metallic atom. For example, anomalous results, recognisable by unexpected colours and solubilities of the products, are often met with among halogeno-, amino-, and even ketonic acids.

An unusual phenomenon has been observed in some cases, for example, that of cobalt benzoate octammine, namely, that when once obtained, the ammines are stable at temperatures much above that at which alone they can be produced.

In the following list of hydrates and ammines, the temperatures given in brackets are those at which the vapour pressures are 760 mm., that is, they are the "dissociation temperatures" on which the author bases his comparisons of stability.

Benzoates.—Nickel; *hexahydrate*, pale green leaflets; *octammine* ($-1.5°$). Cobalt; *tetrahydrate*, grey with a tinge of pink, changes to the bluish-violet anhydrous salt at 115°; *octammine* (32·5°, but can only be prepared at about $-20°$). Copper; the peacock-blue anhydrous salt becomes first violet, then copper-coloured, then dark blue, further greenish-blue and green, and finally forms the grey *octammine* ($-5.5°$); the tensions of the blue *hexammine* (14°), red *tetrammine* (82·5°), and violet *diammine* (183°), are given in place of incorrect data quoted earlier (A., 1916, ii, 104). Manganese; *dihydrate*, very pale pink; *octammine* (10·5°). Zinc; *diammine* (190°), *tetrammine* (57°), *hexammine* (18°), *octammine* ($-2.5°$). Cadmium; *diammine* (182°), *tetrammine* (42°), *hex-*

ammine (17·5°), *octammine* (6°). Ferrous; *trihydrate*, groups of pale green prisms; *octammine* (7°).

Benzenesulphonates.—Nickel; *hexahydrate*, microscopic, rhombic leaflets; *hexammine* (145·5°), bluish-violet. Copper; *hexahydrate*, very pale greenish-blue, silky; *pentammine*, smalt-blue. Zinc; *hexahydrate*, microscopic, rhombic leaflets; *tetrammine* and *pentammine*.

Sulphanilates.—The copper salt is very sparingly soluble, olive-brown when cold, dark brown at 100°, and forms *penta-* and *hexa-ammines* (blue). Nickel; *tetrahydrate*, pale bluish-green prisms; *hexammine* and *octammine* (below 0°), both pale reddish-violet.

Phthalates.—The pale blue copper salt forms a *hexammine*. Nickel; *dihydrate*, brilliant green; *hexammine*.

Trinitrobenzoates.—Copper; *dihydrate;* reddish-brown ammines and an almost black *decammine* (the abnormal additive capacity is partly due to the participation of the nitro-groups).

o-Naphthoylbenzoates.—Nickel; *decahydrate*, very pale pink, not green, as most nickel salts; *hexammine* and *octammine* (15°). Copper; *tetra-* and *hexa-hydrates*, almost white; *octammine* (2°). Zinc; *octammine* (−6°).

Naphthalates.—Copper; *tetrahydrate*, slender, pale blue needles; *hexammine* (about 0°) and *tetrammine*, both pale slate-grey. Zinc; *tetrammine*.

α-Naphthalenesulphonates.—Nickel; *trihydrate*, very pale green; *tetra-* and *hexa-ammines.* Copper; *trihydrate*, almost snow-white, although the solution is deep green and the anhydrous salt pale yellowish-brown; *di-* and *tri-ammines.*

β-Naphthalenesulphonates.—Nickel; *nonahydrate*, green; *hexammine*, white; *octammine* (26°), very pale violet. Cobalt; *hexahydrate*, almost colourless; *octammine* (18·5°). Copper; *hexahydrate*, blue; *hexammine* (79·5°); *octammine* (−1°). Zinc; *hexahydrate*, silky leaflets; *octammine* (1·5°). Cadmium; *hexahydrate*; *hexammine* (90·5°). Ferrous; *hexahydrate*, leaflets; *octammine* (−10°). Manganese; *hexahydrate*, almost colourless; *octammine* (3·5°).

Dibromonaphthalene-β-sulphonates.—These are usually so very sparingly soluble that the acid might find application in analysis. Nickel, pearl-grey, forms a *hexammine* (above 150°) and *octammine* (0°). Copper, reddish-violet, forms a *tetrammine.*

Nitroprussides.—Zinc; *trihydrate;* *tetrammine* and *octammine* (−5°). J. C. W.

Hydrogenation of Aromatic Compounds by the Help of Platinum. III. Hydrogenation with Platinum containing Oxygen. RICHARD WILLSTÄTTER and DANIEL JAQUET (*Ber.*, 1918, **51**, 767—779).—As the application of platinum in the catalytic hydrogenation of organic compounds has developed, various authors have found that it sometimes makes a difference whether the metal is entirely free from oxygen at the commencement of a reduction or has been freely exposed to the air. In many cases, no difference

can be observed, for example, in the reduction of benzene by platinum black (A., 1912, i, 545), but Hess has found that the careful exclusion of oxygen is of great importance in the hydrogenation of pyrrole and certain derivatives (A., 1913, i, 1378). The present paper describes cases of the opposite nature, in which the metal needs to be " primed " occasionally with oxygen, and the conclusion is drawn that platinum itself and platinum loaded with oxygen are distinct catalysts.

A similar difference was observed by Purgotti and Zanichelli (A., 1904, ii, 329), who found that platinum free from air would not induce the decomposition of hydrazine, whilst ordinary platinum preparations will do so, but would cause the decomposition of hydrogen peroxide and hydroxylamine The particular case now dealt with, however, is the hydrogenation of the anhydrides of *o*-dicarboxylic acids. For example, phthalic anhydride suffers practically no reduction in glacial acetic acid unless the apparatus is opened as occasion requires and the platinum-black is shaken with the air, when the reduction proceeds from stage to stage quite smoothly, the final products being hexahydrophthalide (mixed with a little *o*-hydroxymethylhexahydrobenzoic acid), hexahydro-*o*-toluic acid (a mixture of *cis*- and *trans*-isomerides), and hexahydrophthalic acid. The initial products include phthalide and *o*-toluic acid, which indicates that the anhydride ring is more readily attacked than the benzene nucleus, but in the case of phthalimide, which can only be hydrogenated in glacial acetic acid solution with the best spongy platinum (not necessarily activated by oxygen), the sole product is *hexahydrophthalimide*, $\mathrm{\begin{matrix} CH_2 \cdot CH_2 \cdot CH \cdot CO \\ CH_2 \cdot CH_2 \cdot CH \cdot CO \end{matrix}}\!\!>\!\!NH,$ monoclinic prisms, m. p. 132°.

Naphthalic anhydride also can only be hydrogenated by platinum which is activated from time to time by oxygen. The products include a tetra- and a deca-hydronaphthalide, decahydroacenaphthene, $C_{12}H_{20}$, and a *tetrahydro-1-methylnaphthalene-8-carboxylic acid*, needles, m. p. 150°.

The influence of such anhydrides on the reduction of the corresponding acids, and even benzene, is remarkable. Unless the precaution of activating the catalyst with oxygen is taken, hydrogenations that would otherwise proceed smoothly are inhibited by traces of these anhydrides. Thus, if phthalic acid is quite free from its anhydride, and naphthalic acid is freshly precipitated from an alkaline solution, they may be reduced to hexa- and tetrahydro-derivatives, respectively, under ordinary conditions, but not otherwise. *iso*Phthalic acid usually contains traces of phthalic anhydride, which inhibits reduction, but may be reduced to a mixture of *cis*- and *trans*-hexahydro-acids if pure and suspended in glacial acetic acid. *p*-Toluic acid readily yields *cis*- and *trans*-hexahydro-acids.

Indole is readily reduced in glacial acetic acid, the final product being *perhydroindole (octahydroindole)*, which is an alkaline oil with an unpleasant odour, b. p. 182—183°/720 mm., 65°/

12 mm., D_4^{20} 0·9947, and forms a *platinichloride*, m. p. 172—173°, and a *picrate*, m. p. 137—138°. Partial hydrogenation gives a mixture of indole with di- and per-hydroindoles. The perhydroindole may be extracted by shaking the ethereal solution with 0·1N-hydrochloric acid, and the other products separated by fractional precipitation with ethereal picric acid. The yellow picrate of the dihydro-base is formed first, and then the red salt of indole itself, and the change in colour is quite distinct at the point of contact of the two liquids. J. C. W.

Acetylaminophenyl Salicylate. Preparation of Salophen.

R. Q. BREWSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1136—1138).— An investigation of the causes of the poor yields obtained in the preparation of salophen. The reduction of the crude *p*-nitrophenyl salicylate must be effected in non-aqueous solution to prevent hydrolysis of the ester and its reduction product; with glacial acetic acid and zinc dust, the yield of *p*-aminophenyl salicylate is 45% of the theoretical. When this is acetylated without being isolated, the yield of crude salophen, m. p. 175—180°, is 60% of the theoretical.

Using purified *p*-nitrophenyl salicylate, the yield of *p*-aminophenyl salicylate is increased to 73%, and that of salophen to 80%, of the theoretical. [See *J. Soc. Chem. Ind.*, 1918, 530A.]

C. S.

A New Group of *cyclo*Propane Derivatives. II. Action of some Analogues of Phenacyl Haloids on 3-Acylcoumarins.

OSKAR WIDMAN (*Ber.*, 1918, **51**, 907—911. Compare this vol., i, 347).—The reaction described in the first paper is found to be common to other aryl halogenomethyl ketones.

Thus, *p*-chloroacetylanisole (*p*-methoxyphenyl chloromethyl ketone) reacts with 3-acetylcoumarin in the presence of sodium ethoxide to form 3-*acetyl*-3 : 4-*anisacylidenecoumarin*,

$$\begin{matrix} C_6H_4-CH \\ O\cdot CO\cdot CAc \end{matrix} > CH\cdot CO\cdot C_6H_4\cdot OMe,$$
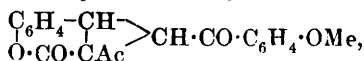
which crystallises in long needles, m. p. 163°, and *ethyl* α-*acetyl-αβ-anisacylidenecoumarinate* [*ethyl* 1-*acetyl*-2-*p*-*methoxybenzoyl-*3-*o*-*hydroxyphenyl*cyclo*propane*-1-*carboxylate*],

$$OMe\cdot C_6H_4\cdot CO\cdot CH < \begin{matrix} CAc\cdot CO_2Et \\ CH\cdot C_6H_4\cdot OH \end{matrix}$$
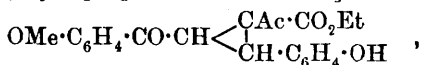
which separates from benzene in long, flat prisms with $1C_6H_6$, m. p. 70°, or 119—120° when free from solvent benzene.

3-Benzoylcoumarin yields 3-*benzoyl*-3 : 4-*anisacylidenecoumarin*, long, pointed prisms, m. p. 190°, whilst ethyl coumarin-3-carboxylate forms *ethyl* 3 : 4-*anisacylidenecoumarin*-3-*carboxylate*, prisms, m. p. 165—166°, and *ethyl* 2-*p*-*methoxybenzoyl-*3-*o*-*hydroxyphenyl*cyclo*propane*-1 : 1-*dicarboxylate*, m. p. 99—100°.

The ethyl 3 : 4-anisacylidenecoumarin-3-carboxylate is hydrolysed

by 4% sodium hydroxide to *α-hydroxy-γ-p-methoxybenzoyl-α-o-hydroxyphenylpropane-ββ-dicarboxylic acid,*

$$OH \cdot C_6H_4 \cdot CH(OH) \cdot C(CO_2H)_2 \cdot CH_2 \cdot CO \cdot C_6H_4 \cdot OMe,$$

short prisms, m. p. 119—120°, and *anisacylmalonic acid,*

$$OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot CH(CO_2H)_2,$$

which crystallises in stellate groups of needles, m. p. 162° (decomp.), and may be synthesised by condensing *p*-chloroacetylanisole with ethyl sodiomalonate.

o-Chloroacetylanisole yields *3-acetyl-3 : 4-o-methoxyphenacylidene-coumarin,* prisms, m. p. 144—145°; ω-bromo-*m*-nitroacetophenone gives rise to *ethyl* 3 : *4-m-nitrophenacylidenecoumarin-3-carboxylate,* prisms, m. p. 162—163°, and *ethyl 2-m-nitrobenzoyl-3-o-hydroxy-phenyl*cyclo*propane-1 : 1-dicarboxylate,* large, hard crystals, m. p. 132—133°; and 1-chloroacetylnaphthalene (α-naphthyl chloro-methyl ketone, b. p. 204—205°/18 mm.) produces *3-acetyl-3 : 4-α-naphthacylidenecoumarin,* hard prisms, m. p. 133—134°.

<div align="right">J. C. W.</div>

Some New Derivatives of *p*-Coumaric and Vanillic Acids. FRITZ VON KONEK and EUGEN PACSU (*Ber.*, 1918, **51**, 855—865). —Some years ago, Konek synthesised methyl 3-amino-6-benzoyl-oxybenzoate hydrochloride and found that it had a cocaine-like effect (*Math.-Naturwiss. Anz. Akad. Wiss., Budapest,* **14**, 16). The synthesis has now been extended to other phenolic acids in order to test the influence of the kind and position of the various groups on the physiological activity.

p-Coumaric (*p*-hydroxycinnamic) acid, from *p*-hydroxybenz-aldehyde by Perkin's method, is converted into the methyl ester, and this is treated with *p*-nitrobenzoyl chloride and sodium hydr-oxide solution. The *methyl* p-4′-*nitrobenzoyloxycinnamate,* rosettes of silky, white needles, m. p. 203°, is reduced by means of tin and alcoholic hydrogen chloride to *methyl* p-4′-*aminobenzoyl-oxycinnamate,* $NH_2 \cdot C_6H_4 \cdot CO_2 \cdot C_6H_4 \cdot CH \colon CH \cdot CO_2Me$, which has m. p. 168—169°, and forms a very sparingly soluble *hydrochloride,* long needles, decomp. 215°, and sulphate.

For the preparation of another ester, *β-p*-nitrophenylpropionic acid was required. This is prepared as follows: *β*-phenylpropionic acid (hydrocinnamic acid) is dissolved in about ten times its weight of fuming nitric acid at 85°, the solution is poured into ice-water, and the crude product dissolved in about fifty times its weight of boiling water and then cooled to 65°, whereby the *p*-nitro-acid separates almost pure, leaving the *o*-nitro-acid to crystallise on cooling further. About 63% of the parent acid is converted into the para-derivative and 30% into the ortho-compound by this means. The desired acid is treated with thionyl chloride, and the *β-p-nitrophenylpropionyl chloride,* b. p. 189—192°/16 mm., m. p. 34—35°, is treated with methyl *p*-hydroxycinnamate, whereby *methyl* p-*β*-4′-*nitrophenylpropionoxycinnamate* is formed, in white needles, m. p. 131—132°. This is reduced to *methyl* p-*β*-4′-*amino-phenylpropionoxycinnamate,*

$$NH_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot C_6H_4 \cdot CH \colon CH \cdot CO_2Me,$$

which crystallises in long needles, m. p. 153—154°, and forms a sparingly soluble *hydrochloride*, decomp. 250°.

5-Nitrovanillic acid (Vogl, A., 1899, i, 697) is converted by means of thionyl chloride into the chloride, *5-nitro-4-hydroxy-3-methoxybenzoyl chloride*, m. p. 93—94°, this into the *methyl* ester, pale yellow, glistening needles, m. p. 148—149°, and then into *methyl 5-nitro-4-benzoyloxy-3-methoxybenzoate*, pale yellowish-brown needles, m. p. 124—125°, by means of benzoyl chloride and pyridine. This ester is reduced to *methyl 5-amino-4-benzoyloxy-3-methoxybenzoate*, $OBz \cdot C_6H_2(NH_2)(OMe) \cdot CO_2Me$, which crystallises in needles, m. p. 188—190°, and forms a sparingly soluble *hydrochloride*, decomp. 236—240°.

Neither of the above amino-acid esters has any effect on the epidermis or tongue. J. C. W.

Some Piperylhydrazones. ALBERT WEINHAGEN (T., 1918, **113**, 585—587).—A description of the condensation products of several aldehydes and ketones with piperylhydrazine, the latter being obtained by the reduction of nitrosopiperidine.

Piperonalpiperylhydrazone, $C_{13}H_{16}O_2N_2$, forms colourless needles, m. p. 65—67°; *salicylaldehydepiperylhydrazone*, $C_{12}H_{16}ON_2$, needles, rhombic plates, or octahedra, m. p. 71—72°; *formaldehydepiperylhydrazone*, $C_6H_{12}N_2$, prismatic needles, m. p. 78—79°; benzaldehydepiperylhydrazone, pentagonal or hexagonal plates, m. p. 68—69° (compare Forster, T., 1915, **107**, 267); *anisaldehydepiperylhydrazone*, $C_{13}H_{18}ON_2$, hexagonal plates, m. p. 54°; p-*hydroxybenzaldehydepiperylhydrazone*, $C_{12}H_{16}ON_2$, m. p. 161°; p-*aminoacetophenonepiperylhydrazone*, $C_{13}H_{19}N_3,H_2O$, prismatic crystals, m. p. 108° With *iso*valeraldehyde, a small quantity of a *substance*, m. p. near 122°, was obtained, whilst with propionaldehyde, acetone, p-aminobenzaldehyde, dextrose, galactose, and *l*-xylose the products were resinous. D. F. T.

Attempt to Synthesise Fisetol. J. TAMBOR and EDMOND M. DU BOIS (*Ber.*, 1918, **51**, 748—751).—*m*-Dimethoxybenzene is condensed with bromoacetyl bromide under the influence of aluminium chloride, and thus converted into 2-*hydroxy-4-methoxyphenyl bromomethyl ketone* (ω-*bromoresacetophenone methyl ether*), $OH \cdot C_6H_3(OMe) \cdot CO \cdot CH_2Br$, which crystallises in stout prisms, m. p. 92° (compare A., 1905, i, 916, and Auwers and Pohl, A., 1914, i, 981). The corresponding *chloro*-compound forms white needles, m. p. 119°, and the *iodo*-derivative separates in very pale yellow prisms, m. p. 102°. If the bromo-ketone is heated with sodium acetate and acetic anhydride, it yields the *diacetate* (glistening scales, m. p. 86°) of 2-*hydroxy-4-methoxyphenyl hydroxymethyl ketone*, this being obtained in colourless plates, m. p. 128°, by hydrolysis with alcoholic potassium hydroxide. The latter is the methyl ether of fisetol, but no method has been devised whereby the methoxyl group can be exchanged for hydroxyl. J. C. W.

Pungent Principles of Ginger. I. Zingiberone. (A Correction.) HIROSHI NOMURA (*Sci. Rep. Tohôku Imp. Univ.*, 1918, **6**, 375).—The ketone, isolated from ginger, to which, in a previous paper (*ibid.*, 1917, **6**, 41), the name zingiberone was assigned, bears no relation to the zingiberol obtained by Brooks (A., 1916, i, 408), and in order to avoid confusion the name zingerone is substituted for zingiberone (compare T., 1917, **111**, 769; Lapworth, Pearson, and Royle, *ibid.*, 777). H. M. D.

Oxidation of Diaminophenols. JEAN PICCARD and LOUIS M. LARSEN (*J. Amer. Chem. Soc.*, 1918, **40**, 1079—1092).—Holoquinonoid aminobenzoquinoneimine salts have been prepared with the purpose of comparing their colours with those of other holoquinonoid and of meriquinonoid salts. It is found that the auxochromic effect of an anilino-group is, unlike the cases of other holoquinonoid salts, the same as that of a dimethylamino-group. *2-Amino-p-benzoquinone-4-imine hydrochloride*,

$$O\!:\!C_6H_3(NH_2)\!:\!NH,HCl,$$
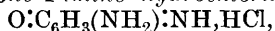
which separates when an aqueous solution of 2 : 4-diaminophenol dihydrochloride is oxidised by $4N$-ferric chloride at $0°$, and the solution is further cooled to $-15°$, crystallises in two forms, unstable, pale red needles and stable, dark red plates with a green surface colour; it is rapidly decomposed by water, is proved to be holoquinonoid by titration with titanium trichloride, forms red solutions in water or alcohol, which are changed to yellow by concentrated sulphuric acid owing to salt-formation at the amino-group, and gives a spectrum showing general absorption in the violet region. The quinonoid *perchlorate* was obtained in pale red needles (not quite pure) which exploded violently when heated. The quinonoid *nitrate* was obtained by oxidising with $2N$-ferric nitrate instead of with $4N$-ferric chloride; it is more stable than the hydrochloride and exists in only one modification, bright red needles. *2-Dimethylamino-p-benzoquinone-4-imine perchlorate*, $O\!:\!C_6H_3(NMe_2)\!:\!NH,HClO_4$, is obtained by oxidising 4-amino-2-dimethylaminophenol dihydrochloride with $4N$-ferric chloride at $0°$, adding a saturated solution of sodium perchlorate, and cooling to $-20°$; it crystallises in pale red needles which slowly darken on keeping, forms violet-red solutions, is unchanged by strong acids except concentrated sulphuric acid, in which it dissolves to a pale yellow solution, becoming violet-red again on dilution, and gives a flat absorption curve with a wide maximum in the green. The *picrate* crystallises in long, dark brown needles, and forms red solutions in alcohol and acetone.

3-Amino-6-hydroxydiphenylamine, colourless crystals which rapidly oxidise in air, obtained by the electrolytic reduction of *m*-nitrodiphenylamine in concentrated sulphuric acid (1·5 amps., 6·5 volts, electrode 15 sq. cm.), is isolated as the *dihydrochloride*, unstable, hygroscopic crystals, which in 50% acetic acid at $0°$ is oxidised by $4N$-ferric chloride, the addition of picric acid in glacial acetic acid to the resulting violet solution yielding *2-anilino-p-*

benzoquinone-4-imine picrate, $O:C_6H_3(NHPh):NH,C_6H_2(NO_2)_3\cdot OH$. This salt forms a microcrystalline powder, yields red solutions in alcohol and acetone, and dissolves in dilute acids, forming violet solutions. Salts with the usual inorganic acids have not been obtained, on account of their instability in solution.

An orthoquinonoid structure of the preceding quinoneimine salts is not impossible. C. S.

Syntheses by Means of Sodamide. Preparation and Study of some·Monoalkyl and Dialkylcamphors and their Derivatives. A. HALLER and JEAN LOUVRIER (*Ann. Chim.*, 1918, [ix], **9**, 189—251).—For the most part a more detailed account of work already published (compare A., 1914, i, 555). The following new compounds are described. *Diethylcampholamide*, m. p. 75°, b. p. 185°/12 mm., $[a]_D^{15} + 76°15'$ to 77°5', prepared by the action of sodamide on diethylcamphor in xylene, when acted on by nitrous acid yields *diethylcampholic acid*, m. p. 78°, b. p. 157°/20 mm., $[a]_D^{15} + 60°59'$ to 62°49', giving a *potassium* salt. *Methylethylcampholamide*, m. p. 60°, b. p. 180°/14 mm., $[a]_D^{15} + 75°42'$ to 73°55', yields *methylethylcampholic acid*, m. p. 74°, $[a]_D^{15} + 57°10'$ to 55°24'.

Allylborneol, b. p. 119°/14 mm., $[a]_D^{16} + 19°23'$ to 20°22', gives a *phenylurethane*, m. p. 64°.

Diallylcamphor, b. p. 155°/16 mm., D_0^0 0·982, $[a]_D^{17} + 148°$ to 152°22'; *diallylborneol*, m. p. 47°, $[a]_D^{18} + 78°28'$; *diallylcampholamide* or $4(2' : 2' : 3')$-*trimethyl*cyclo*pentyl-2-methyl-4-allylpyrrolidone*, $NH_2\cdot CO\cdot C_8H_{14}\cdot CH(C_3H_5)_2$ or

$$NH\Big<{}^{CHMe\cdot CH_2}_{CO-\!-\!-\overset{|}{C}(C_3H_5)\cdot CH}\Big<{}^{CMe_2\cdot \overset{|}{C}HMe}_{CH_2-\!-\overset{}{C}H_2}.$$
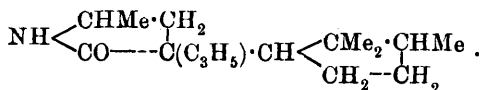
b. p. 212°/15 mm., $[a]_D^{18} 40°18'$.

Dibenzylcampholamide, m. p. 121°, $[a]_D^{19} + 33°7'$ to 34°18'.

Benzylethylcampholamide, m. p. 181°, b. p. 230—240°/12 mm.

Ethylcampholenonitrile, b. p. 110°/11 mm., D_0^0 0·903, $[a]_D^{13} + 70°26'$, gives in turn *ethylcampholenamide*, m. p. 62°, and *ethylcampholenic acid*, m. p. 36°, b. p. 157°/20 mm.

Allylcamphoroxime, m. p. 101°, b. p. 158°/16 mm., $[a]_D^{14} + 58°10'$ to 54°14', gives a *phenylurethane*, m. p. 160°, and yields in turn *allylcampholenonitrile*, b. p. 130°/11 mm., D_0^0 0·934, $[a]_D^{14} + 28°47'$; *allylcampholenamide*, m. p. 97°; and *allylcampholenic acid*, m. p. 49°, b. p. 156°/16 mm.

Propylcamphoroxime yields *propylcampholenonitrile* b. p. 124°/11 mm., D_0^0 0·907, $[a]_D^{16} + 46°18'$; *propylcampholenamide*, b. p. 173°/12 mm.; and *propylcampholenic acid*, b. p. 160°/12 mm.

Benzylcamphoroxime gives *benzylcampholenonitrile*, b. p. 195°/14 mm., $[a]_D^{17} + 54°14'$ to $+43°58'$, according to the method of preparation; *benzylcampholenamide*, b. p. 197°/12 mm., and *benzylcampholenic acid*, m. p. 68°, b. p. 204°/12 mm., which gives a *sodium* salt. W. G.

The Wagner Rearrangement. L. RUZICKA (*Helvetica Chim. Acta*, 1918, **1**, 110—133).—It is shown that whilst methyl-α-fenchocamphorol and methylcamphenilol apparently do not undergo the Wagner rearrangement when heated with sodium hydrogen sulphate, methylborneol and methylfenchyl alcohol, despite their marked difference in structure, give the same reaction products after the removal of water, namely, fenchone and camphor. These results go to show that of the two possible explanations of the Wagner rearrangement, that demanding the intermediate formation of a tricyclene ring is the more correct. The apparent contradiction underlying this explanation can be elucidated in the following way, and a further proof of the tricyclene theory advanced at the same time. Whereas the tricyclenes derived from borneol and fenchyl alcohol are different substances, it is found that the tricyclenes obtained from their homologues, methylborneol and methylfenchyl alcohol, must be identical. It is therefore clear that in this case the further products of the reaction must also be identical. The formation of this common tricyclene from compounds of the fenchone and camphor types is to be attributed to the fact that the single linkings of the tricyclene three-membered ring exhibit different stabilities towards sodium hydrogen sulphate. Generally, the linking which leads to the fenchone type is opened, whilst that leading to the camphor type is more stable; the third linking, which would lead to an unknown type, is not opened. A consideration of the tricyclenes obtainable from the other alcohols shows that otherwise quite different isomeric alcohols yield the same tricyclene. This will explain why methylcamphenilol apparently does not undergo rearrangement on removing water. The tricyclene obtained is identical with that furnished by borneol, and consequently the only product of the reaction is camphene. With regard to the further rupture of the three-membered ring of the tricyclene, the author gives the following generalisations:

(1) Of the linkings of the three-membered ring of the tricyclenes, that is the weakest which lies between the two carbon atoms where the difference between the numbers of directly connected hydrogen atoms is greatest.

(2) Should two bonds be similar in the above respect, then that one will be opened which at the same time opens the five-membered ring with the largest number of quaternary carbon atoms.

A number of tables showing the relationships are included in the paper.   J. F. S.

Constituents of Resins. I. Siaresinol from Siamese Gum Benzoin. ALOIS ZINKE and HANS LIEB (*Monatsh.*, 1918, **39**, 95—105).—Siaresinol from Siamese gum benzoin (Reinitzer, A., 1915, i, 431) is probably identical with the benzoresinol obtained by Lüdy from the same source (A., 1893, i, 666); it gives an *additive* compound with acetic acid, $C_{30}H_{48}O_4,C_2H_4O_2$, needles, m. p. 280--281·5° and a *benzoyl* derivative, needles, m. p.

182—183°, $[\alpha]_D^{20} + 30\cdot0°$ (ethyl alcohol), which on hydrolysis regenerates siaresinol. D. F. T.

The Isolation of Pigments by Means of Picric and Dichloropicric Acids. RICHARD WILLSTÄTTER and GUSTAV SCHUDEL (*Ber.*, 1918, **51**, 782—788).—In devising a method for the extraction of plant pigments, Willstätter has already had a certain measure of success with a process which depends on the partition of the dye between water and amyl alcohol (compare A., 1917, i, 42—50). The serious limitation to this method is that only non-glucosidic pigments are efficiently extracted, diglucosides often being left entirely in the aqueous layer. If picric acid is added to the solution, a wider range of pigments can be transferred, as picrates, to other, non-miscible solvents. Thus, ether will only dissolve the picrates of non-glucosidic pigments; diethyl ketone will not remove the diglucoside picrates, but extracts monoglucoside picrates to the extent of about 50% of the quantity present; whilst a mixture of amyl alcohol (2 parts) and acetophenone (1 part) will remove all the monoglucosides and 70—80% of the diglucosides as picrates.

The use of picric acid has this drawback, however, that the picrates are usually not very soluble in organic media. Dichloropicric acid is much superior in this respect, although it is so much more soluble in water that the expenditure of reagent is greater. By the use of this acid, rosaniline and pararosaniline can be completely extracted from aqueous solutions by ether; safranine by diethyl ketone; methylene-blue by ether, the picrate crystallising soon in bronzy prisms; and mono- and di-glucosidic pigments can be removed completely by one extraction with a mixture of amyl alcohol and acetophenone (2:1).

No actual example of the use of dichloropicric acid is given, but the occasion serves to describe its preparation. *p*-Nitroaniline is chlorinated by Flürscheim's method (T., 1908, **93**, 1772), the 2:6-dichloro-4-nitroaniline is converted into 3:5-dichloro-1-nitrobenzene (Holleman, A., 1905, i, 41), and this is reduced to the amine by means of iron filings and hydrochloric acid, and then transformed into 3:5-dichlorophenol, which is nitrated by means of fuming nitric acid and acetic acid. Dichloropicric acid (3:5-dichloro-2:4:6-trinitrophenol) crystallises in pale yellow prisms, m. p. 139—140° (corr.) (compare Blanksma, *Rec. trav. chim.*, 1908, **27**, 25, 36), the sodium salt in quadratic prisms, and the potassium salt in slender needles, both being lemon-yellow. The solubilities in water at 19·7° are 7·4, 7·4, and 0·55 grams per 100 c.c., for the acid, Na and K salt, respectively.

The conversion of 3:5-dichloroaniline into 3:5-dichlorophenol is carried out by adding the solution of the diazonium sulphate to a boiling mixture of concentrated sulphuric acid, water, and anhydrous sodium sulphate (proportions, 9:5:6). If Blanksma's method is adopted (*ibid.*), the following by-products arise: 3:5-

dichloro-4-3′ : 5′-*dichlorobenzeneazophenol*, brownish-red, flat, silky prisms, m. p. 191—192° (corr.), and 3 : 5-*dichloro*-2 : 4-*bis*-3′ : 5′-*dichlorobenzeneazophenol*, $OH \cdot C_6HCl_2(N:N \cdot C_6H_3Cl_2)_2$, long, glistening, orange needles, m. p. 260—261° (corr.), both of which form sodium salts which dissolve in ether; and 3 : 5-*dichloro*-4-*nitrosophenol*, very pale greenish-yellow prisms, m. p. 150—151° (corr.).

<div align="right">J. C. W.</div>

Isomerism of Furfurylidenediacetyl Monoxime [β-2-Furylvinyl Acetyl Ketoxime]. Otto Diels and Hermann Roehling (*Ber.*, 1918, **51**, 828—836. Compare A., 1913, i, 875).—The product of the condensation of furfuraldehyde with dimethyl diketone monoxime, namely, β-2-furylvinyl acetyl ketoxime, yields an *acetate*, $C_4H_3O \cdot CH:CH \cdot CAc:N \cdot OAc$, prisms, m. p. 141°, which is transformed by warming with 33% potassium hydroxide into the salt of β-2-furylacrylic acid, $C_4H_3O \cdot CH:CH \cdot CO_2H$.

When added to concentrated hydrochloric acid, the oxime rapidly dissolves with a deep olive-green colour, changing to brown, and then deposits crystalline leaflets of the *hydrochloride*, decomp. 128—129°, of an isomeric *base*, which is supposed to be formed by the hydrolytic rupture of the furan ring, followed by ring closure in a new position, thus:

$$\begin{array}{ccc} CH \cdot CH & & CH \cdot CH \\ CH \ C \cdot CH:CH \cdot C \cdot COMe + H_2O & \rightarrow & CH \ C \cdot CH:CH \cdot C \cdot COMe \\ \diagdown \diagup \qquad HO \cdot N & & OH \ OH \quad HO \cdot N \\ O & & \end{array}$$

$$\downarrow -H_2O$$

$$OH \cdot CH:CH \cdot CH:C{\displaystyle <}{{CH:CH} \atop {O——N}}{\displaystyle >}C \cdot COMe.$$

(or $CHO \cdot CH_2 \cdot CH:C<$)
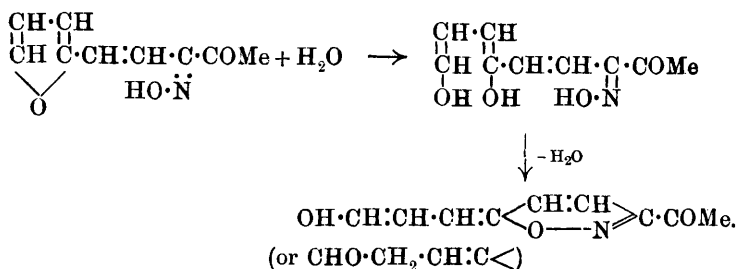
The base crystallises in greenish-yellow needles, m. p. 145°, dissolves in concentrated hydrochloric acid and in dilute alkali hydroxides or carbonates, reduces Fehling's and ammoniacal silver solutions immediately, gives a deep violet-red coloration with alcoholic ferric chloride, which soon disappears, owing to reduction, but remains permanganate-coloured on adding an excess of the reagent, forms a deep red compound with benzenediazonium chloride, and yields the following characteristic derivatives: (*a*) with methyl chloroformate, a *carbomethoxy*-compound, white needles, m. p. 128—129°; (*b*) a p-*nitrophenylhydrazone*, brownish-red, slender, curved needles, decomp. 136—137°; (*c*) with methylamine, a *product*, $C_{10}H_{12}O_2N_2$, pale yellow needles, m. p. 175° (decomp.), and a substance crystallising in stout, chromate-red rhombohedra, m. p. 183°. When boiled with an excess of water or dilute sulphuric acid, or heated with methyl iodide at 100°, the base changes into a third isomeride, namely, 3-*acetyl*-5-2′-*furyl*-4 : 5-

*dihydro*isoo*xazole*, $C_4H_3O \cdot CH {<} {\overset{CH_2 \cdot \overset{\text{Ac}}{\underset{\|}{C}}}{\underset{O——N}{}}}$, which crystallises in soft, white needles, m. p. 103—104°. J. C. W.

β-Phenylcoumarins. ADOLF SONN (*Ber.*, 1918, **51**, 821—827). —Some years ago, von Meyer stated that 3-hydroxyflavone is produced when benzoacetodinitrile, $NH\!:\!CPh \cdot CH_2 \cdot CN$, is condensed with resorcinol under the influence of hydrogen chloride (A., 1903, i, 482). It is known that dinitriles of this type readily change into acylacetonitriles on treatment with acids, and therefore it might be expected that the above result would be achieved if ω-cyanoacetophenone, $COPh \cdot CH_2 \cdot CN$, were substituted for the dinitrile. Bargellini and Forli-Forti have already studied the condensation of compounds of this type with phenols, and proved that the products are β-phenylcoumarins and not flavones. This led the author to suspect that von Meyer had wrongly interpreted his result, and he has found, on repeating the experiment, that the product is not 3-hydroxyflavone, but 7-hydroxy-4-phenylcoumarin (Pechmann and Hancke, A., 1901, i, 210).

In their condensations, Bargellini and Forli-Forti used zinc chloride, and were not very successful. It is better to dissolve the materials in glacial acetic acid and to employ hydrogen chloride as the condensing agent. Thus, *p*-cyanoacetylanisole and phloroglucinol yield 5 : 7-*dihydroxy-4-p-methoxyphenylcoumarin*, which crystallises in flat prisms, m. p. 262°, and forms a *diacetate*, glistening, elongated tablets or flat prisms, m. p. 189—190° (the Italian authors gave m. p. 179—180°). If ether is used as solvent, a different product is formed, most probably the corresponding *imino-ether*, $C_6H_2(OH)_2 {<} {\overset{O————C\!:\!NH}{\underset{C(C_6H_4 \cdot OMe)\!:\!CH}{}}}$, stout, pale yellow crystals, decomp. above 300°, since it yields the coumarin on warming with water or dilute acids.

The dinitrile corresponding with *p*-cyanoacetylanisole, namely, *p-methoxybenzimidoacetonitrile*, $OMe \cdot C_6H_4 \cdot C(\!:\!NH) \cdot CH_2 \cdot CN$, is obtained in colourless, stout prisms, m. p. 119°, by the interaction of anisonitrile and acetonitrile in the presence of sodium, the primary sodium salt being decomposed by water. J. C. W.

Synthesis of Ketones in the Thiophen Series. V. THOMAS and V. COUDERC (*Bull. Soc. chim.*, 1918, [iv], **23**, 288—291).— Magnesium thienyl iodide reacts with nitriles, giving products which when treated with water give good yields of ketones. The following have been prepared by this method : ethyl thienyl ketone ; phenyl thienyl ketone, dithienyl ketone ; *α-naphthyl thienyl ketone*, b. p. 187—188°/25 mm.; and *β-naphthyl thienyl ketone*, colourless needles, m. p. 87°. W. G.

Synthesis of 1-Methyltetrahydropyridinecarboxylic Acids. I. A New Method for Preparing Arecaidine and Arecoline. Elucidation of the Constitution of Guvacine and Arecaine. KURT HESS and FRIEDRICH LEIBBRANDT (*Ber.*, 1918, **51**, 806—820). —When the 1-methylpiperidinecarboxylic acids are brominated in

methyl or ethyl alcohol and the products are heated with sodium alkyl oxides, 1-methyltetrahydropyridinecarboxylic acids are produced. These are closely related to the alkaloids of the areca (betel) nut.

Nipecotinic acid (piperidine-3-carboxylic acid) forms a fairly stable *acetate*, needles, m. p. 289—290° (decomp.). The following new derivatives of 1-methylpiperidine-3-carboxylic acid (compare A., 1917, i, 354) have been prepared : from the methyl ester (dihydroarecoline), the *hydrochloride*, needles, m. p. 193° (decomp.) ; methiodide, prismatic plates, m. p. 192° ; and methoaurichloride, m. p. 123° (compare Willstätter, A., 1897, i, 385) ; also the *ethyl* ester, b. p. 101—102°/24 mm., and green *copper* salt.

Methyl 1-methylpiperidine-3-carboxylate is converted as indicated above into methyl 1-methyl-1 : 2 : 5 : 6-tetrahydropyridine-3-carboxylate, which is identical with arecoline, as the corresponding free acid is identical with arecaidine. The latter forms a *hydrobromide*, needles, m. p. 197° (decomp.).

Two other areca-nut alkaloids have been registered, namely, guvacine and its *N*-methyl derivative, arecaine (Jahns, A., 1891, 94, 1520). Assuming that these must be closely related to arecaidine, the authors have prepared 1-methyl-1 : 4 : 5 : 6-tetrahydro-pyridine-2-carboxylic acid from 1-methylpiperidine-2-carboxylic acid in the same way. This very closely resembles, but is not identical with, arecaine. *Methyl 1-methylpiperidine-2-carboxylate*, from pipecolinic acid acetate (*loc. cit.*), has b. p. 92—95°/21 mm., and the *hydrochloride* of the ethyl ester (*ibid.*) has m. p. 204° (decomp.). *1-Methyl-1 : 4 : 5 : 6-tetrahydropyridine-2-carboxylic acid* crystallises from pure alcohol in well-developed, quadratic, prismatic tablets, m. p. 213—214° (arecaine is insoluble in alcohol and has m. p. 231°), and forms a *hydrochloride*, m. p. 210°, readily soluble in alcohol (arecaine hydrochloride has m. p. 250° and is sparingly soluble), a *platinichloride*, orange-yellow prisms, m. p. 220° (arecaine platinichloride forms octahedra), an *aurichloride*, m. p. 200°, a *methyl* ester, and an *ethyl* ester, b. p. 96°/17 mm., both of which are limpid, highly refractive, pleasant-smelling oils.

The relationship between guvacine and arecaine is definitely established by methylating the former by the author's method, using formaldehyde and formic acid. The pure arecaine and its salts thus obtained had somewhat different properties from those quoted by Jahns ; the new data are given above in brackets. When arecaine is boiled with alcoholic hydrogen chloride, it loses its methyl group and forms the *ethyl* ester of guvacine, b. p. 116°/19 mm., instead of its own ethyl ester. This oil reduces alkaline permanganate and absorbs bromine immediately.

This esterification of arecaine proves one thing, however, namely, that a carboxyl group is present in these alkaloids. That they also contain an ethylene linking is proved by the reduction of guvacine with hydrogen and colloidal platinum, when "dihydroguvacine" is formed. This is identical with *iso*nipecotinic acid (piperidine-4-carboxylic acid). Consequently, guvacine is a tetrahydro-

pyridine-4-carboxylic acid, probably the 1 : 2 : 5 : 6-isomeride, and arecaine is its 1-methyl derivative. J. C. W.

Guvacine Methyl Ester (Guvacoline) and its Occurrence in Nature. KURT HESS (*Ber.*, 1918, **51**, 1004—1006).—The alkaloids of the areca nut include arecaidine and its methyl ester, arecoline, guvacine and its *N*-methyl derivative, arecaine, and also the methyl ester of guvacine, which is designated "*guvacoline.*" A specimen of the *hydrobromide* of this, crystallising in short prisms, m. p. 144—145°, has been provided by Messrs. Merck, and proved to have the above constitution by hydrolysis to guvacine and by esterification of this alkaloid. J. C. W.

Guvacine. KARL FREUDENBERG (*Ber.*, 1918, **51**, 976—982).— Independent of Hess, and without reference to his work (preceding abstracts), the author has investigated guvacine, and draws the conclusion that it is demethylated arecaidine, or 1 : 2 : 5 : 6-tetra-hydropyridine-3-carboxylic acid. If this is so, then arecaine and arecaidine are identical.

The above acid was synthesised by Wohl and Losanitsch (A., 1908, i, 47), and there is good agreement between the decomposition temperatures of the hydrochlorides, aurichlorides, and platini-chlorides of this and guvacine. Guvacine *methyl ester*, b. p. 114° (corr.)/13 mm., forms a *hydrochloride*, hygroscopic leaflets, m. p. 121—122° (corr.), a *platinichloride*, silky, golden leaflets, m. p. 211° (corr.), and a methiodide. The latter has the same m. p. as arecoline methiodide, and yields arecaidine on hydrolysis, there being again good agreement in the decomposition temperatures of the salts of the natural alkaloid and the present material.

1-p-*Toluenesulphonylguvacine* crystallises in stout plates, m. p. 167—168° (corr.), and is oxidised by alkaline permanganate to a (3 : 4 ?)-*dihydroxy* - 1 - p-*toluenesulphonylpiperidine*-(3 ?)-*carboxylic acid*, leaflets, m. p. 213—214° (corr.; decomp.), and by ozone in 95% acetic acid to a dicarboxylic *acid*, probably of the formula $C_7H_7 \cdot SO_2 \cdot N \begin{cases} CH_2 \cdot CH_2 \cdot CO_2H \\ CH_2 \cdot CO_2H \end{cases}$, which crystallises in prisms and plates, m. p. 164° (corr.). J. C. W.

A New Volatile Alkaloid of the Common Broom. AMAND VALEUR (*Compt. rend.*, 1918, **167**, 163—164. Compare this vol., i, 350).—After separation of the alkaloids sparteine and saro-thamnine (*loc. cit.*) from the mother liquors in the manufacture of sparteine sulphate, a new alkaloid was obtained by the addition of excess of alkali and extraction with ether. The new alkaloid, *genisteine*, $C_{16}H_{28}N_2$, has m. p. 60·5°, b. p. 139·5—140·5°/5 mm. (corr.), 177—178°/22 mm. (corr.), and yields a *hydrate*,

$$C_{16}H_{28}N_2, H_2O,$$

$[\alpha]_D -52·3°$ (in alcohol), a *picrate*, $C_{16}H_{28}N_2, 2C_6H_2(NO_2)_3 \cdot OH$, m. p. 215° (decomp.), a *platinichloride*,

$$C_{16}H_{28}N_2, 2HCl, PtCl_4, 2\tfrac{1}{2}H_2O,$$

*u**

decomposing at 235°, and an *aurichloride,*
$$2(C_{16}H_{28}N_2,2HCl),3AuCl_3,$$
yellow prisms, m. p. 188° (decomp.). This alkaloid is saturated
and does not contain a methyl group attached to nitrogen.

W. G.

**The Alkaloids of the Pomegranate Tree. V. Resolution
of Pelletierine and Methyl*iso*pelletierine into their Optical
Antipodes. Elucidation of Tanret's Bases.** Kurt Hess and
Annaliese Eichel (*Ber.*, 1918, **51**, 741—747. Compare this vol.,
i, 34).—Pelletierine and methyl*iso*pelletierine have been resolved
by means of their tartrates. The bases were first treated with
the *d*-acid, the solutions evaporated in a vacuum desiccator to
syrupy consistency, and then mixed with alcohol, when the salt
of the *d*-base separated, and then the *l*-base was recovered from
the mother liquor and converted into the *l*-tartrate.

d-*Pelletierine* d-*tartrate* has m. p. 129°, $[\alpha]^{20} + 19{\cdot}48°$, and
l-*pelletierine* l-*tartrate* has m. p. 129°, $[\alpha]^{20} - 19{\cdot}62°$. The active
bases suffer considerable racemisation on distillation, but they may
be isolated and converted into solutions of their sulphates with
constant rotation, $[\alpha]^{18} + 5{\cdot}39°$ and $- 5{\cdot}33°$ respectively. d-*Methyl-
iso*pelletierine d-*tartrate* has m. p. 133—134°, $[\alpha]^{20} + 19{\cdot}12°$, and
l-*methyl*isopelletierine l-*tartrate* has m. p. 132—134°, $[\alpha]^{18} - 19{\cdot}37°$.
The free bases, in this case, are not subject to racemisation when
distilled, resembling in this respect the parent alkaloid, coniine.
The difference is probably due to the position of the oxygen atom,
the side-chain being $-CH_2{\cdot}CH_2{\cdot}CHO$ in the case of pelletierine and
$-CO{\cdot}CH_2{\cdot}CH_3$ in the other case. d-*Methyl*isopelletierine has b. p.
109°/24 mm., $[\alpha]^{18} + 6{\cdot}71°$ (solution in *N*-sulphuric acid), $+ 9{\cdot}90°$
(solution in hydrochloric acid), and the l-*base* has practically the
corresponding constants. (The light employed was that of an
incandescent gas lamp.)

Among the alkaloids of the pomegranate, Tanret described some
optically active forms of the above bases, but the rotations reported
by him were much greater than those observed with the resolved
alkaloids. The authors feel quite convinced that no active modifi-
cations are present in the root, for they have not found optical
activity to be displayed by any of their fractions, either before or
after distillation.   J. C. W.

**Degradation of Scopoline. III. Scopoline → Hydro-
scopoline → Tropan.** Kurt Hess (*Ber.*, 1918, **51**, 1007—1015.
Compare A., 1916, i, 285, and Schmidt, *ibid.*).—It has been sug-
gested already that hydroscopoline is a dihydroxytropan. Hydr-
oxytropans are found to resist reduction by ordinary methods, but
when heated with concentrated hydriodic acid and a considerable
excess of phosphonium iodide at 200°, they suffer replacement of
hydroxyl by hydrogen fairly readily. Thus tropine yields tropan
and nortropine gives nortropan, whilst hydroscopoline also forms
tropan, which supports the above assumption.

Of the two oxygen atoms in scopoline, one is known to be present in a hydroxyl group and the other is probably included in an oxide ring. The comparative ease with which scopoline combines with hydrogen bromide and parts with it again on treatment with alkalis suggests the oxidic structure, but there can scarcely be an ethylene–oxide arrangement such as Schmidt proposed, thus, –C·OH

$|{>}O$, as a hydrogen bromide additive compound from this would –CH

be very unstable, which hydroscopoline bromide is not. The author believes that the oxygen atom in question bridges across from the pyrrolidine ring to some carbon atom in the piperidine ring.

When hydroscopoline bromide hydrobromide is boiled with concentrated hydrochloric acid, it yields *hydroscopoline chloride hydrochloride*, $C_8H_{14}O_2NCl,HCl$, needles, m. p. 289° (decomp.). Many attempts have been made to oxidise this salt, in the hope of obtaining a chloroscopolic acid, but, almost always, the only product was found to be scopoline. With silver oxide and hot water, however, the strange result was the elimination of the *N*-methyl group, norscopoline being obtained.

A convenient method for the preparation of hydroscopoline is described.   J. C. W.

The Linear Phenonaphthacridonequinone and Quinacridonequinone. W. St. Lesnianski (*Ber.*, 1918, **51**, 695—706). ––These compounds have been synthesised in order to determine whether quinones of the acridone series resemble anthraquinone derivatives in being vat dyes, which is found to be the case.

Anthranilic acid and α-naphthaquinone are heated together in alcoholic solution, when *o-2-naphthaquinonylaminobenzoic acid* (I) is formed. This crystallises in red needles, m. p. 271° (corr.), forms a dark red *silver* salt, and yields *phenonaphthacridonequinone* (II) on heating with concentrated sulphuric acid at 140—150°.

$$C_6H_4{<}^{CO-C·NH·C_6H_4·CO_2H}_{CO-CH} \qquad C_6H_4{<}^{CO·C·NH}_{CO·C--CO}{>}C_6H_4.$$

(I.)   (II.)
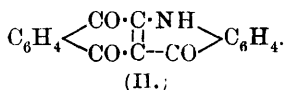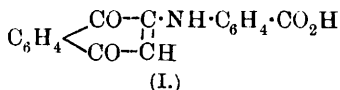
The quinone sublimes in orange needles, m. p. 384°, forms a red *potassium* salt, $C_{17}H_8O_3NK,H_2O$, and gives compounds with various acids, of which the *nitrate*, $B,2HNO_3$, pale yellow needles, is an example. On distillation with zinc dust, it yields dihydrophenonaphthacridine, m. p. 285—286° (Schöpff, A., 1895, i, 107), whilst reduction with sodium hyposulphite gives *dihydrophenonaphthacridonequinone* as a reddish-violet powder, m. p. 317° (corr.), which forms blue solutions in alkali hydroxides, from which cotton is dyed orange-yellow, and yields an orange *acetyl* derivative, m. p. 292° (corr.). *Dinitrophenonaphthacridonequinone*, a yellow powder, m. p. 299° (corr.), is obtained by the action of a warm mixture of fuming nitric and sulphuric acids.

The other quinone is obtained by heating benzoquinonedi-

anthranilic acid (III) (Ville and Astre, A., 1895, i, 465) with sulphuric acid at 145—155°.   *Quinacridonequinone* (IV) is an

$$CO_2H \cdot C_6H_4 \cdot NH \underset{O}{\overset{O}{\bigcirc}} NH \cdot C_6H_4 \cdot CO_2H \qquad C_6H_4 \underset{NH \cdot C \cdot CO \cdot C - CO}{\overset{CO - C \cdot CO \cdot C \cdot NH}{<}} C_6H_4$$

(III.)   (IV.)
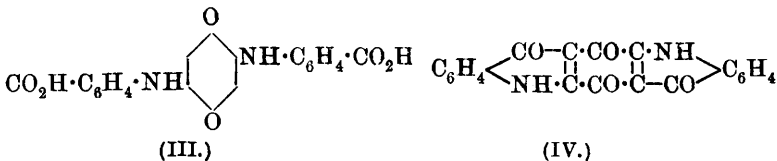
amorphous, yellow powder, which partly sublimes and decomposes, without melting, at above 530°, and is insoluble even in solvents of high b. p. It forms a red, crystalline, *potassium* salt, $C_{20}H_9O_4N_2K,H_2O$, and an amorphous, brownish-yellow, *dipotassium* salt, $C_{20}H_8O_4N_2K_2,H_2O$, both of which are very easily hydrolysed, and it also yields an unstable *nitrate*, $B,4HNO_3$, long, golden-yellow needles, and a crystalline *sulphate*, $B,3H_2SO_4$. The quinone is practically indifferent to the action of alkalis, acylating, or ketone reagents, but yields *dihydroquinacridine*,

$$C_6H_4 \underset{CH_2}{\overset{NH}{<}} C_6H_2 \underset{N}{\overset{CH}{<}} C_6H_4,$$
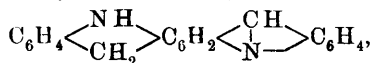
as a dark red, lustrous powder, m. p. 379° (corr.; decomp.), when distilled with zinc dust. It may also be reduced by means of sodium hyposulphite, but the bluish-violet product is insoluble. On warming with fuming nitric acid, it yields *dinitroquinacridone-quinone*, $C_{20}H_8O_4N_2(NO_2)_2$, as a pale yellow, insoluble powder, which forms a dark red *potassium* salt, $2H_2O$.   J. C. W.

Bromoalkylated Aromatic Amines. III. Derivatives of Ethylenediamine. J. von Braun, K. Heider, and E. Müller (*Ber.*, 1918, **51**, 737—741. Compare this vol., i, 107, 269).—The ω-bromoethyl derivatives of secondary amines react with other secondary bases to form compounds of the general formula $C_6H_5 \cdot NR \cdot C_2H_4 \cdot NR'R''$, where R' and R'' may be both aliphatic radicles or one of them aromatic. The nitroso-derivatives of these may be deprived of the aromatic residues by hydrolysis, thus giving rise to alkylated ethylenediamines of the types
$$NHR \cdot C_2H_4 \cdot NHR'$$
or $NHR \cdot C_2H_4 \cdot NR'R''$, some of which are now described. The syntheses are comparatively simple and doubtless of manifold applicability.
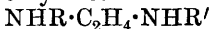
s-Diphenyldimethylethylenediamine (*loc. cit.*, 108) gives a pale green *dinitroso*-compound, $C_2H_4(NMe \cdot C_6H_4 \cdot NO)_2$, m. p. 208°, which forms an almost insoluble, greenish-brown *monohydrochloride*, m. p. 153°, and is hydrolysed by boiling with sodium hydrogen sulphite solution (D 1·21) to *s*-dimethylethylenediamine, m. p. 119° (Schneider, A., 1896, i, 200)

Methyl-β-bromoethylaniline (this vol., i, 108) reacts with ethylaniline or ethyl-β-bromoethylaniline (this vol., i, 270) with methylaniline to form *NN'-diphenyl-N-methyl-N'-ethylethylenediamine*, $NMePh \cdot C_2H_4 \cdot NEtPh$, as a viscous liquid, b. p. 232—234°/21 mm.,

which gives a *picrate*, m. p. 176°, a pp'-*dibromo*-compound, needles, m. p. 100°, and a yellowish-green *dinitroso*-derivative, m. p. 190°. The latter is hydrolysed as above to s-*methylethylethylenediamine*, a mobile oil, b. p. 133°, which fumes in the air and forms a very hygroscopic *hydrochloride*,

$$NHMe\cdot C_2H_4\cdot NHEt,2HCl,$$
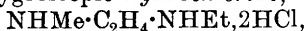
m. p. 217—218°, and a *platinichloride*, m. p. 240°.

Phenyltrimethylethylenediamine (this vol., i, 108) likewise gives rise to *trimethylethylenediamine*, $NHMe\cdot C_2H_4\cdot NMe_2$, which has b. p. 140° (about) and forms a very hygroscopic *hydrochloride*, m. p. 183°, a *platinichloride*, yellowish-red spikes from water, in which it is freely soluble, m. p. 230° (decomp.), and a *dipicrate*, m. p. 209—210°. J. C. W.

New Selenium Derivatives of Antipyrine. FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, **51**, 842—855).—The action of the selenium chlorides on antipyrine is described.

The monochloride reacts as though it were "selenoselenyl dichloride," $Se\dot{:}SeCl_2$. When a solution in carbon tetrachloride is added to a concentrated solution of antipyrine in chloroform at 0°, *diantipyryl diselenide* (or *selenoselenide*),

$$Se\dot{:}Se\dot{:}\left[C\diagdown\begin{matrix}CMe\cdot NMe\\CO-NPh\end{matrix}\right]_2,$$
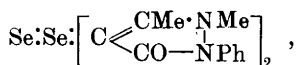
is deposited. This crystallises from about 40% alcohol in yellow needles, m. p. 215—216°, and deposits elementary selenium when boiled with hydrochloric acid, the solution containing the salt of *diantipyryl selenide*. This compound is precipitated by the addition of sodium carbonate; it crystallises from benzene in pearly flakes, m. p. 240°, and forms a *dihydrochloride* and a *compound* with mercuric chloride. It may be identical with a substance mentioned in D.R.-P. 299510 (1917), obtained from antipyrine by the action of selenium dioxide and concentrated sulphuric acid.

Selenium tetrachloride also reacts vigorously, giving *diantipyrylselenium dichloride*, $(C_{11}H_{11}ON_2)_2SeCl_2$, which crystallises from benzene in pearly scales, m. p. 225°, and changes into the above selenide on treatment with alkalis.

Some notes on the analysis of organo-selenium compounds are given in an appendix. For the estimation of carbon and hydrogen, the long combustion tube is filled with copper oxide and lead chromate in equal layers, with a layer of lead peroxide, about 12—15 cm. long, kept at 180—200°, in the front. The various methods for estimating selenium have been tested, but not one is found to be entirely satisfactory. Oxidation with nitric acid or nitric acid and potassium chlorate is accompanied by loss of selenium in the fumes; for the oxidation by sodium peroxide, a large excess of the reagent must be used, otherwise some free selenium will be obtained, and the quantitative reduction of the sodium selenate formed to the element cannot be achieved; combustion in oxygen in a bomb sometimes results in loss by the

alloying of selenium with the platinum wires and alec the production of oxides other than the desired selenic oxide (see this vol., ii, 309). Frerich's method (decomposition with fuming nitric acid in the presence of silver nitrate, evaporation, filtration of the silver selenite, and titration of this in dilute nitric acid solution by means of a thiocyanate solution) gave correct results in the above cases, but it was also found to be convenient to digest the compound with pure sulphuric acid (10 c.c. for 0·2 gram) until a brownish-green colour developed, then to dilute to about 200 c.c., saturate with sulphur dioxide, leave overnight, and collect the precipitate of selenium. The drawback to this method is that it is difficult to tell just when to stop the action of the sulphuric acid, as it must not proceed to the production of much selenious acid.

<div align="right">J. C. W.</div>

Synthesis of some New Naphthylpyrazolones. FRITZ VON KONEK and RICHARD MITTERHAUSER (*Ber.*, 1918, **51**, 865—871).— The application of some naphthylhydrazines in the synthesis of pyrazolones is described.

β-Naphthylhydrazine and ethyl benzylacetoacetate produce 1-*β-naphthyl-4-benzyl-3-methyl-5-pyrazolone* (I), which crystallises in rosettes of pale pink needles, m. p. 153°, yields a *picrate*, canary-yellow, matted needles, and reacts with benzoyl chloride in the presence of sodium hydroxide solution to form the benzoate of its enolic modification, namely, 5-*benzoyloxy-1-β-naphthyl-4-benzyl-3-methylpyrazole* (II), yellow needles, m. p. 138°. The same base
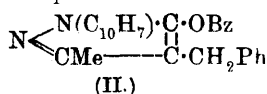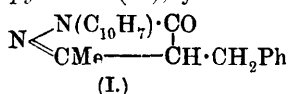
reacts with ethyl *iso*propylacetoacetate to form 1-*β-naphthyl-3-methyl-4-isopropyl-5-pyrazolone*, small, pale yellow needles, m. p. 160° (*picrate*, yellow needles), and with crotonic acid to give 1-*β-naphthyl-3-methyl-5-pyrazolidone*, pale brown crystals, m. p. 107°. Aceto-β-naphthylhydrazide (from the base and acetamide) reacts with ethyl benzylacetoacetate and phosphorus trichloride to form 1-*β-naphthyl-4-benzyl-5-methyl-3-pyrazolone*, yellow needles, m. p. 208°.

α-Naphthylhydrazine gives rise to 1-*α-naphthyl-4-benzyl-3-methyl-5-pyrazolone*, pale yellow rosettes, m. p. 168°, which forms a yellow *picrate* and reacts with nitrous acid to yield a *bis-pyrazolone*,
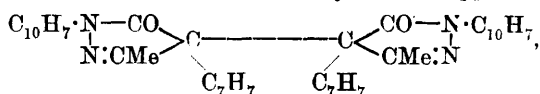
brown crystals, m. p. 215°.

pp'-Dihydrazinodiphenyl and ethyl benzylacetoacetate condense at 160° to form 4 : 4′-*diphenylenebis-4-benzyl-3-methyl-5-pyrazolone*, $C_{34}H_{30}O_2N_4$, as a yellow powder.   J. C. W.

Synthesis of Iminouracil-6-acetic Acid. DAVID E WORRALL (*J. Amer. Chem. Soc.*, 1918, **40**, 1133—1135).—Guanidine carbonate and ethyl acetonedicarboxylate readily condense in boiling alcoholic solution to give a 90% yield of *guanidine 2-iminouracil-6-acetate*, $NH{<}^{CO\text{———}CH}_{C(:NH)\cdot NH}{>}C\cdot CH_2\cdot CO_2H,CH_5N_3$, microscopic needles, decomp. 213—214° with formation of an amorphous solid, m. p. 230°. A solution of the salt forms with a solution of copper sulphate dark green, diamond-shaped crystals. *2-Iminouracil-6-acetic acid*, liberated from the guanidine salt by hydrochloric acid, crystallises from water in colourless, square plates, m. p. 289—290° (decomp.), decomposes soluble carbonates, reacts with bromine to form a *substance*, needles, m. p. 210—211° (decomp.), and with concentrated nitric acid at 70° to form an amorphous, yellow 5-*nitro*-derivative, decomp. 309—310°. The sodium salt and copper sulphate solution yield a light green precipitate consisting of microscopic, pointed, twinned plates intersecting at right angles.

C. S.

Hydrogen Peroxide as a Reagent in the Purine Group. II. Action of Hydrogen Peroxide on Uric Acid. C. S. VENABLE (*J. Amer. Chem. Soc.*, 1918, **40**, 1099—1120. Compare Venable and Moore, this vol., i, 104).—The usual course of the experiments is to treat an aqueous solution of uric acid with a definite volume of 6N-sodium hydroxide, to bring the mixture to the desired temperature, and to add the hydrogen peroxide, usually in 3% solution. At definite intervals, samples are taken and analysed. The temperature range is 20—90°, and the excess alkali concentration from 0 to 0·5N. Three different products are formed, according to the experimental conditions. In weakly alkaline or neutral solutions and at temperatures near that of boiling water, allantoin is first formed in large quantities, together with smaller amounts of carbonyldicarbamide, but no genetic relationships connecting the two substances have been discovered; they appear to be products of two independent reactions. As the oxidation proceeds, the amount of carbonyldicarbamide remains fairly constant, but the yield of allantoin rapidly diminishes, with the appearance of increasing amounts of cyanuric acid up to a maximum yield of 10%. Increasing the alkalinity at this high temperature rapidly diminishes the yield of all three substances, until with an excess alkalinity of 0·1N only very small amounts of cyanuric acid are obtained. At lower temperatures and in weakly alkaline solutions the same phenomena were observed, the disappearance of the allantoin being much slower. On increasing the ·alkalinity, the yield of cyanuric acid rapidly increased, with a corresponding decrease in the yields of both allantoin and carbonyldicarbamide. At 20° and with an excess alkalinity of 0·5N, no allantoin or carbonyldicarbamide was observed, whilst the yield of cyanuric acid was as high as 50% of the theoretical. Further increase of alkalinity or lowering of the temperature was apparently without effect   The

preceding high yield of cyanuric acid required explanation, because it was found that under the experimental conditions allantoin was rapidly decomposed by hydrogen peroxide without producing cyanuric acid, and the largest yield of carbonyldicarbamide was 15%, which, assuming a quantitative conversion to cyanuric acid and adding the 10% of the latter already present, only accounts for a 30% yield of cyanuric acid. Furthermore, the conversion of 1 mol. of carbonyldicarbamide to 1 mol. of cyanuric acid requires the liberation of 1 mol. of ammonia, whereas the molecular ratio of ammonia formed to cyanuric acid recovered was found to be less than 1:3. Also, in all oxidations at low temperature and high excess of alkali, no allantoin or carbonyldicarbamide was obtained throughout the course of the oxidation (twenty-four hours), and carbonyldicarbamide, oxidised under similar conditions, was not entirely converted into cyanuric acid even after forty-eight hours. These facts indicate that the oxidation of uric acid by hydrogen peroxide at low temperatures and high excess of alkali is fundamentally different from that occurring at high temperatures and a low concentration of alkali, and that some intermediate product must exist in the alkaline solution after oxidation, which is decomposed during the acidification, constituting the first step in the analysis of the products. To test this point, the alkaline solution resulting from the oxidation was treated with manganese dioxide to destroy the excess of hydrogen peroxide, and was then neutralised by acetic acid, whereby a 60% yield of a mixture of the normal and the acid salts of a dibasic *acid*, $C_4H_5O_5N_3$ [*ammonium* salt, $C_4H_3O_5N_3(NH_4)_2$], was obtained. This acid, oxidised in acid solution by hydrogen peroxide, gives an 80% yield of cyanuric acid; it cannot be converted into allantoin, carbonyldicarbamide, or uroxanic acid (see also next abstract).

The formation of cyanuric acid is in all cases a secondary reaction. It may be formed by the alkaline oxidation of allantoin, especially in neutral solution at high temperature, by the action of alkali alone on carbonyldicarbamide, and, in the best yield, from the acid, $C_4H_5O_5N_3$, as above.

Attempts to trace a parallelism between the oxidising action of hydrogen peroxide and of potassium permanganate on uric acid have been unsuccessful.   C. S.

Hydrogen Peroxide as a Reagent in the Purine Group. III. Allantoxanic Acid as an Oxidation Product of Uric Acid. F. J. Moore and Ruth M. Thomas (*J. Amer. Chem. Soc.*, 1918, **40**, 1120—1132. Compare preceding abstract).—The best conditions for preparing Venable's acid, $C_4H_5O_5N_3$, are the oxidation by hydrogen peroxide at the ordinary temperature of an alkaline solution of uric acid, the excess alkalinity of which is approximately normal. The ammonium salt when heated in a sealed tube at 150° is converted almost quantitatively into ammonium carbonate and allantoxaidine, the latter also being formed when the barium salt is treated with a slight excess of

sulphuric acid and the filtrate is evaporated. This suggests that Venable's acid is hydrated allantoxanic acid, $C_4H_3O_4N_3,H_2O$, and the suggestion is confirmed by the identity of its ammonium salt with ammonium allantoxanate prepared by Ponomarev's method and by its reduction to hydroxonic (dihydroallantoxanic) acid by sodium amalgam.

In the formation of allantoxanic acid from uric acid by hydrogen peroxide, neither allantoin nor glycol-uril is an intermediate product. The oxidation of allantoxanic acid to cyanuric acid by hydrogen peroxide in acid solution does not pass through allantoxaidine. C. S.

Acetyl-p-diazoimides Derived from Substituted p-Phenylenediamines. GILBERT T. MORGAN and DAVID ALEXANDER CLEAGE (T., 1918, **113**, 588—596).—The general nature of the reaction by which acyl-p-diamines can be converted into acyl-p-diazoimides, although indicating the considerable influence of the acyl group on the intramolecular condensation, nevertheless does not preclude the possibility of isolating the parent substances of this series of diazo-compounds. Derivatives of p-phenylenediamine containing acidic substituents in the nucleus have therefore been submitted to examination.

2-Nitro-p-phenylenediamine in dry acetone reacts with nitrous anhydride, yielding 3-*nitro*-p-*phenylene*-1-*diazo*-4-*imide*,

$$\mathrm{NH{:}C}{<}^{\mathrm{C(NO_2){:}CH}}_{\mathrm{CH{=\!=}CH}}{>}\mathrm{C}{<}^{\mathrm{N}}_{\mathrm{N}},$$
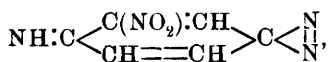
a brown, crystalline solid which becomes resinous when warmed to the ordinary temperature. The *acetyl* derivative of this substance, brownish-red plates, which explode at 140°, combines with β-naphthol, with formation of 3-*nitro*-4-*acetylaminobenzeneazo*-β-*naphthol*, $\mathrm{NHAc{\cdot}C_6H_3(NO_2){\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH}$, a dark red powder, m. p. above 290°; this substance on hydrolysis gives 3-*nitro*-4-*aminobenzeneazo*-β-*naphthol*, a pale brown powder, m. p. 208°, which after further diazotisation reacts with β-naphthol, producing a *bisazo*-derivative, and with hot alcohol producing 3-*nitrobenzene-azo*-β-*naphthol*, orange crystals, m. p. 192°. The identity of the last substance, which serves to confirm the constitution ascribed to the above nitroacetylphenylenediazoimide, is demonstrated by direct comparison with a specimen synthesised from m-nitroaniline. Further evidence as to the constitution is adduced by the preparation of the isomeric 2-*nitro*-4-*acetyl*-p-*phenylene*-1-*diazo*-4-*imide*, $C_8H_6O_3N_4$, decomp. 142° (with explosion), by the interaction of 2-nitro-4-acetyl-p-phenylenediamine and nitrous anhydride in dry acetone; this combines with β-naphthol, giving rise to 2-*nitro*-4-*acetylaminobenzeneazo*-β-*naphthol*, a red substance, m. p. 298°, the hydrolysis of which yields 2-*nitro*-4-*aminobenzeneazo*-β-*naphthol*. By further diazotisation, this product can be made to combine again with β-naphthol, giving a bisazo-compound, and also to undergo reduction by hot alcohol to 2-nitrobenzeneazo-β-naphthol, the

identity of which is also confirmed by direct comparison with a specimen prepared from *o*-nitroaniline.

In a similar manner, 2 : 6-dichloro-*p*-phenylenediamine is found to react with nitrous anhydride in dry acetone, giving unstable 3 : 5-*dichloro*-p-*phenylene*-1-*diazo*-4-*imide*, which yields a more stable 4-*acetyl* derivative, a grey, crystalline powder, decomp. 138° with explosion. This acetyl derivative gives colour reactions with the naphthols and naphthylamines identical with those exhibited by the yellow 3 : 5-dichloro-4-acetyl-*p*-phenylene-1-diazo-4-imide, decomp. at 133°, obtained by diazotising 2 : 6-dichloro-1-acetyl-*p*-phenylenediamine, and the suggestion is made that the almost colourless and yellow forms of the acetyl compound may be represented by the cyclic diazoimide constitution, $C_6H_2Cl_2{<}^{NAc}_{N_2}$, and the diazoquinoneimide constitution, $NAc{:}C_6H_2Cl_2{<}^{N}_{N}$ respectively, the difference disappearing on combination with phenols or bases. 2 : 6-*Dichloro-4-acetyl*-p-*phenylene*-1-*diazo-4-imide*, $C_8H_5ON_3Cl_2$, almost colourless plates, decomp. at 138°, obtained from 2 : 6-dichloro-4-acetyl-*p*-phenylenediamine, is to be regarded as probably of cyclic diazoimide structure. D. F. T.

Compounds Derived from Proteins by Energetic Treatment with Nitric Acid. F. KNOOP (*Zeitsch. physiol. Chem.*, 1918, **101**, 210—211. Compare Mörner, this vol., i, 198).—The unidentified acid substances discovered by Mörner (*loc. cit.*) amongst the oxidation products of protein are probably 5-nitroglyoxaline-4-carboxylic acid, $C_4H_3O_4N_3$ (Windaus and Opitz, A., 1911, i, 752), and glyoxaline-4-glyoxylic acid, $C_5H_4O_3N_2$ (Knoop, A., 1907, i, 788). Both substances are oxidation derivatives of histidine and have the properties described by Mörner. Attention is directed to the fact that the latter substance, $C_5H_4O_3N_2$, must contain either 2 or 4 atoms of hydrogen instead of 3 (as found by Mörner) if it consists of a simple molecule. H. W. B.

Preparation of Ovalbumin, and its Refractive Indices in Solution. A. R. C. HAAS (*J. Biol. Chem.*, 1918, **35**, 119—125).—The crystallisation of ovalbumin is found to be dependent on the hydrogen ion concentration of the globulin-free solution of white of egg; crystals are formed in the presence of ammonium sulphate when the hydrogen ion concentration lies between 10^{-5} and 10^{-6}.

The refractive indices of solutions of ovalbumin in water, 1% ammonium sulphate, and in various concentrations of sodium hydroxide obey the law $n-n_1=a{\times}c$, where n is the observed refractive index of the protein solution, n_1 that of the solvent, c the percentage of dissolved protein, and a a constant, which is found to be $0.00177{\pm}0.00006$. The corresponding constant for the albumins of ox serum is $0.00177{\pm}0.00008$ (Robertson, A., 1912, ii, 611). H. W. B.

Preparation of Pure Caseinogen. Lucius L. Van Slyke and John C. Baker (*J. Biol. Chem.*, 1918, **35**, 127—136).—The caseinogen is prepared from undiluted milk by treatment with normal acid, preferably lactic or a mixture of 1 part of hydrochloric and 2 parts of acetic acid. The acid is introduced slowly into the milk below the surface, the tip of the tube carrying the acid being so arranged that it is very close to a mechanical stirrer revolving at a high speed and also near the bottom of the vessel containing the milk. Under these conditions, the acid does not cause coagulation of the caseinogen at the point where the acid first comes into contact with the milk.

The product, the preparation of which requires only about ten hours, is a fine, white powder containing 0·10% of ash and 0·80% of phosphorus. It is free from inorganic phosphorus, calcium, and hydrolytic products of protein, and dissolves at once in dilute solutions of monoacidic alkalis to a clear solution. H. W. B.

Constitution of the True Nucleic Acids. R. Feulgen (*Zeitsch. physiol. Chem.*, 1918, **101**, 288—295. Compare this vol., i, 85, and Levene and Jacobs, A., 1912, i, 926).—A theoretical paper in which the general arrangement of the nucleotides in nucleic acid suggested by Levene is accepted, although the precise method of linking together of the nucleotides is regarded as unsettled (compare also Jones and Read, A., 1917, i, 232, 233).
H. W. B.

Preparation and Properties of Thymic Acid. R. Feulgen (*Zeitsch. physiol. Chem.*, 1918, **101**, 296—309).—Thymic acid is prepared by treating sodium nucleinate with a slight excess of sulphuric acid and keeping the mixture for forty minutes at 80°. The acid is separated in the form of its barium salt, and on hydrolysis yields cytosine and thymine. H. W. B.

Influence of Normal Salts, Bases, and Acids on the Precipitability of Gelatin by Alcohol. Jacques Loeb (*J. Biol. Chem.*, 1918, **34**, 489—501. Compare this vol., i, 240).—In these experiments, finely powdered gelatin is treated for an hour with solutions of normal salts, bases, or acids of various concentrations; the excess of the solution is in each case washed away with water, a 1% solution of the washed gelatin in water being then prepared and treated with alcohol until precipitation just occurs. It is found that when the concentration of the salt solution exceeds a certain limit, which is about $M/128$ in the case of normal salts with univalent anions and cations and monoacidic bases, the gelatin becomes non-precipitable by alcohol, whilst in the case of normal salts with bivalent anion and univalent cation, and also in the case of strong monobasic acids, the concentration at which non-precipitability occurs is just twice as great, namely, $M/256$. After treatment with solutions of normal salts with bivalent cations and univalent or bivalent anions, the gelatin remains precipitable

with alcohol for all the concentrations of the salt used. These experiments confirm the conclusions previously drawn by the author in former papers (*loc. cit.*).   H. W. B.

Action of Pancreatic Enzymes on Casein. H. C. SHERMAN and DORA E. NEUN (*J. Amer. Chem. Soc.*, 1918, **40**, 1138—1145).—A comparative study of the hydrolysis of casein by various preparations derived from the pancreas. Extraction of high-grade commercial pancreatin with 50% alcohol leaves a residue having about the same proteolytic activity as the original pancreatin. The "sac precipitate" which settles out of the amylase solution during the dialysis in 50% alcohol preceding the final precipitation of the amylase preparation (Sherman and Schlesinger, A., 1912, i, 815; 1915, i, 604) has fifteen times the proteolytic activity of the original pancreatin and about four times that of the most active commercial trypsin. The final preparation of pancreatic amylase, purified as described previously (*loc. cit.*), has proteolytic activity fully as great as that of high-grade trypsin.   C. S.

Enzyme Chemis'ry. H. VON EULER (*Zeitsch. Elektrochem.*, 1918, **24**, 173—177).—In the inversion of sucrose by yeast, it is shown that the invertase increases to a maximum and the formation of the enzyme follows the formula $dx/dt = k(a - x)$. Other experiments on the hydrolysis of starch by the enzyme of *Mucor mucedo* are described; in this case, the velocity of the formation of the enzyme is constant.   J. F. S.

The Law of Action of Sucrase. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1918, **167**, 208—210).—The inversion of sucrose by sucrase does not obey Wilhelmy's law, $x = a(1 - e^{-kt})$, at concentrations of sucrose exceeding 2% or 3%, but there is probably a definite ratio of sucrose to sucrase below which the law holds good. Using 5 c.c. of a very active sucrase preparation, the authors have obtained results in agreement with the law up to concentrations of 2% of sucrose.   W. G.

Chemical Reaction in the System : Urea–Urease. EIICHI YAMAZAKI (*J. Tokyo Chem. Soc.*, 1918, **39**, 125—184).—Ammonium carbamate has always been found by Fenton's method in the product of the action of urease on urea. It may therefore be presumed that the decomposing action of urease is a successive hydrolysis of urea, $NH_2 \cdot CO \cdot NH_2 \longrightarrow NH_2 \cdot CO_2 \cdot NH_4 \longrightarrow (NH_4)_2CO_3$, in opposition to the view of the formation of an intermediate product of urea and urease.

The experiments were always carried out in a slightly acidic solution obtained by saturating the reacting system with carbon dioxide. Notwithstanding the phase difference of the two constituents of the reaction, it seems to be a homogeneous chemical reaction, because stirring has no effect on its velocity. The velocity constant k_1 of the first hydrolysis was determined by the initial

velocity, and the constant k_2 of the second hydrolysis by some trials. With a $0.02N$-solution of urea and a solution of urease containing 0.2 gram in 100 c.c., the values obtained were $k_1 = 0.0068$, $k_2 = 0.00617$ at $25°$. These constants vary proportionately to the concentration of the urease. A good coincidence was obtained between the observed values for the velocity of the reaction and the values for k_1 and k_2 calculated by the formula derived from Rakowski's general theory of unimolecular successive chemical reactions (A., 1907, ii, 74). The temperature coefficient of this reaction is 2 per $10°$ between $15°$ and $35°$. Many reagents are adsorbed by urease and show a poisonous action; the action of alkali hydroxide is reversible, whilst that with hydrochloric acid, mercuric chloride, or silver sulphate is irreversible. S. H.

Synthesis of Organic Sodium Derivatives. ANTONIO MADINAVEITIA and JOSE RANEDO (*Anal. Fis. Quim.*, 1918, **16**, 142—145).—Dimethylaniline reacts with mercuric acetate to form dimethylaniline mercury acetate, $Me_2N\cdot C_6H_4\cdot Hg\cdot CO_2Me$, which is transformed by sodium hyposulphite into mercury pp-tetramethyldiaminodiphenyl, $(Me_2N\cdot C_6H_4)_2Hg$. The solution of this substance in benzene reacts with sodium, the mercury being replaced by the alkali metal. The mechanism of the process is similar to the formation of sodium phenyl by the interaction of sodium and mercury phenyl. The sodium compound is spontaneously inflammable on contact with air. A. J. W.

Simplified Method for the Preparation of Tin Triaryl Haloids. ERICH KRAUSE (*Ber.*, 1918, **51**, 912—914).—If the tin tetra-aryls are brominated in ordinary organic media, or alone, no matter how carefully the conditions are controlled, the main products are the tin diaryl dibromides. If the compounds are suspended in pyridine chilled by means of solid carbon dioxide, however, bromination can be stopped at the first stage. The product is freed from solvent and bromobenzene (or analogous compound) by distillation, then transferred to ether, and shaken with 30% sodium hydroxide. The tin triaryl hydroxide dissolves in ether, and can be converted into any desired haloid by means of the acids.

Tin triphenyl chloride, $SnPh_3Cl$, m. p. $106°$, b. p. $240°/13.5$ mm. (compare Aronheim, A., 1879, 250, 651), *bromide*, fern-like groups of octahedra, m. p. $120.5°$, b. p. $249°/13.5$ mm., and *iodide*, large, snow-white, quadratic, monoclinic prisms, m. p. $121°$, b. p. $253°$ 13.5 mm., have been prepared in this way in yields amounting to 90—95%. J. C. W.

Physiological Chemistry.

Comparative Study of the Influence of Carbohydrates and Fats on the Nutritive Power of Alimentary Proteins. F. MAIGNON (*Compt. rend.*, 1918, **167**, 172—175. Compare this vol., i, 359).—Feeding experiments with rats, using diets of egg-albumin and fat, or egg-albumin and starch, or a mixture of the three, indicate that the albumin is better utilised with the fat than with starch, and that the minimum of albumin necessary is much lower with fat than with starch. The most satisfactory mixture of albumin and fat is in the proportion 1:1, even if starch is present.
W. G.

The Nutritive Equilibrium of the Animal Organism. JULES AMAR (*Compt. rend.*, 1918, **167**, 241—242).—The author points out that Maignon's results for fat and starch as supplements to protein in feeding rats (compare preceding abstract) are in opposition to those of Atwater and Benedict (compare A., 1903, ii, 308) and Mendel and Lewis (A., 1913, i, 1406). He directs attention to his own work in this connexion (compare *Moteur humain*, 1909, 289). W. G.

Nitrogenous Metabolism of the Central Nervous System. ELSE HIRSCHBERG and HANS WINTERSTEIN (*Zeitsch. physiol. Chem.*, 1918, **101**, 212—222. Compare this vol., i, 52).—The isolated spinal cord of the frog contains in the fresh material 1·30% of nitrogen, and 1·25% in cords freed from the outer membranes. The content of nitrogen is unaltered by preservation of the cords in air or oxygen, but falls rapidly when immersed in oxygenated saline solution. The addition of a trace of a calcium salt to the saline solution increases the rate of loss of nitrogen from the cord; potassium salts decrease it. Treatment with 4% of alcohol practically arrests nitrogenous metabolism; electrical stimulation increases it nearly fourfold. The katabolic action is an oxidative one. because it fails to occur in the absence of free oxygen.
H. W. B.

Utilisation of various Saccharides in the Metabolism of the Central Nervous System. ELSE HIRSCHBERG (*Zeitsch. physiol. Chem.*, 1918, **101**, 248—254. Compare Hirschberg and Winterstein, this vol., i, 52).—Maltose and sucrose are not utilisable for the maintenance of the metabolic processes of the surviving spinal cords of frogs. Dextrose and lævulose have about equal power in maintaining metabolism in the resting state, whilst lactose has less and galactose considerably more, probably due to the participation of the latter substance in the composition of nervous tissue. During excitation, the consumption of dextrose by the tissue greatly exceeds that of any other saccharide other than

galactose. Dextrose is therefore the best material to supply for the rapid production of power for the use of nervous tissues.

H. W. B.

Oxidation Catalysts in the Animal Organism. Action of certain Ferments on Oxydones. LEOPOLDO LÓPEZ PEREZ (*Anal. Fis. Quim.*, 1918, **16**, 397—421).—A full account of work of which a preliminary note has appeared (see this vol., i, 88).

Origin of Creatine. III. L. BAUMANN and H. M. HINES (*J. Biol. Chem.*, 1918, **35**, 75—82).—Perfusion of dog muscle with choline or sarcosine leads apparently to the production of creatine. Arginine, histidine, betaine, methylguanidine, and cyanamide when similarly treated do not yield any notable increase in the amount of creatine in muscle or urine.

H. W. B.

Amino-acids of Mature Human Placenta. VICTOR JOHN HARDING and CHARLES ATHERTON FORT (*J. Biol. Chem.*, 1918, **35**, 29—41).—The amount of arginine in human placenta is twice as much as that present in any other human organ (liver, heart, kidney, muscle).

H. W. B.

Caseinogen of Human Milk. A. W. BOSWORTH and LOUISE A. GIBLIN (*J. Biol. Chem.*, 1918, **35**, 115—117).—Caseinogen prepared from human milk resembles the caseinogen prepared from cows' and goats' milk in the following respects: It has the same nitrogen, phosphorus, and sulphur content, the same molecular weight and degree of valency; it gives the same series of salts with bases; it is acted on by rennin in the same manner, producing the same casein.

H. W. B.

Free Lactic Acid in Sour Milk. LUCIUS L. VAN SLYKE and JOHN C. BAKER (*J. Biol. Chem.*, 1918, **35**, 147—178).—Lactic acid exists in sour milk largely as lactate, but partly as free acid, some of the latter being in solution, whilst a smaller part is adsorbed by the caseinogen or casein. Sterilised milk inoculated with *Bacterium lactis acidi* does not show the presence of free lactic acid until about twenty hours after the inoculation; the amount then rapidly increases and reaches about 20 c.c. of $0.1N$-acid in forty-eight hours. The p_H value changes from 6·5 in fresh milk to 4·17 in forty-eight hours. The caseinogen begins to coagulate when the p_H reaches 4·64 to 4·78. During the coagulation process, the hydrogen-ion concentration remains constant, although the acidity by titration increases slightly. About 20% of the free lactic acid in coagulated sour milk is adsorbed by the casein.

The first perceptible sign of souring in milk is a characteristic flavour, discernible to the senses of both taste and smell, due to the presence of a volatile compound formed in the souring process, and not to lactic acid. There does not appear to be any relation between either hydrogen-ion concentration or acidity by titration and the first sign of this flavour.

Various methods are described for estimating the free lactic acid and of that portion of it which is adsorbed by the caseinogen or casein.   H. W. B.

Glycerides of Butter Fat. CONRAD AMBERGER (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 313—381).—Butter fat contains only a small quantity (2·4%) of triolein, the greater part of the oleic acid existing in the fat in the form of mixed glycerides. If the oleic acid is present as triolein, the fat when hydrogenised should yield a corresponding quantity of tristearin, but such is not found to be the case. Butyric and other volatile acids are also present in the fat as mixed glycerides; tributyrin cannot be isolated. Examination of the alcohol-soluble portion of hydrogenised butter fat shows that the original fat contains butyrodiolein, butyropalmito-olein, and oleodipalmitin. The author has also isolated from butter fat a glyceride, m. p. 67·9°, and yielding mixed fatty acids, m. p. 55·5°.   W. P. S.

Transformation of Tetrahydronaphthalene (Tetralin) in the Animal Body. G. SCHROETER and K. THOMAS (*Zeitsch. physiol. Chem.*, 1918, **101**, 262—275).—Tetrahydronaphthalene fed to a dog is absorbed and eventually excreted in combination with urea. The existence of four compounds of tetrahydronaphthalene and carbamide is theoretically possible, and the authors have succeeded in preparing all of them by the interaction of potassium cyanate on the respective amines in aqueous solution. ar-*Tetrahydro-α-carbamidonaphthalene*, $C_{11}H_{14}ON_2$, crystallises in square plates from alcohol, softens at 198°, and melts at about 206° (quickly heated, at 212°); ar-*tetrahydro-β-carbamidonaphthalene*, needles from water, m. p. 134° (decomp.); ac-*tetrahydro-α-carbamidonaphthalene*, needles, m. p. 210·5°; ac-*tetrahydro-β-carbamidonaphthalene*, needles, m. p. 183°. Comparison of the natural product with these compounds shows that tetralin in its passage through the body is converted into *dl-ac*-tetrahydro-α-carbamidonaphthalene.

In the preparation of the *ar-β*-compound, a small amount of a substance was obtained in the form of colourless needles, which did not melt below 245° and possessed the composition of *di*-ar-*tetrahydro-β-naphthylcarbamide*, $(C_{10}H_{12}N)_2CO$.   H. W. B.

Relation between the Chemical Structure of the Opium Alkaloids and their Physiological Action on Smooth Muscle with a Pharmacological and Therapeutic Study of some Benzyl Esters. I. Relation of the Chemical Structure of the Opium Alkaloids to their Action on Smooth Muscle. DAVID I. MACHT (*J. Pharm. Expt. Ther.*, 1918, **11**, 389—417).— The results indicate that in respect to their physiological action on the rhythmic contraction and tonicity of smooth muscle from various organs, the opium alkaloids can be divided into two classes: (1) the morphine group; (2) the papaverine group. Members of

the first group, containing a pyridine–phenanthrene nucleus, exert a stimulating action which appears to be associated with the pyridine or piperidine component of the molecule, whilst the members of the papaverine or benzyl*iso*quinoline group exert an inhibitory action which can be traced to the benzyl radicle. Alkaloids such as benzylmorphine or peronine, containing both significant groupings, have an anomalous action on smooth muscle.

H. W. B.

Pharmacology of the Vitamines. FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 419—456).—The administration of vitamines to cats and dogs, either subcutaneously, intravenously, or by the mouth, causes a marked stimulation of the salivary, sweat, gastric, and other glands which is inhibited by atropine. The author considers that the vitamines in the food play an essential part in the processes of digestion and metabolism through their stimulatory action on glands producing external and internal secretions. The commercial vitamine preparation "orypan," obtained from rice husks, was chiefly employed, but similar results were given in some experiments by extracts of oats, meat, yeast, etc. H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Occurrence of Methylpentosans in Cereals and Legumes.

Kintarō Ōshima and Kinsuke Kondō (*J. Tokyo Chem. Soc.*, 1918, **39**, 294—300).—On account of incompleteness of the method of determination of methylpentosans, there has been doubt as to their occurrence in some seeds in which they have been reported to exist. The authors have therefore examined certain cereals and legumes by their improved method (this vol., ii, 338), and have found methylpentosans in all varieties of the soja bean, whilst it is absent in the cereals investigated. S. H.

Phytochemistry of the Crowberry (Empetrum nigrum).

L. van Itallie (*Pharm. Weekblad*, 1918, **55**, 709—717).—The leaves of *Empetrum nigrum* contain a wax composed wholly, or in great measure, of ceryl cerotate, benzoic acid, urson, tannin, dextrose, and probably rutin. The anhydrous urson has the formula $C_{10}H_{16}O$, and is identical with the derivative obtained from the leaves of *Uva Ursi*.

Empetrum nigrum contains no alkaloids, andromedotoxins, or glucosides decomposed by emulsin. The presence of benzoic acid and urson points to a probable relationship between the *Empetraceæ* and *Eriaceæ*. A J. W.

Plant Sterols. I. Sterol Content of Wheat (Triticum sativum). MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 160—172). —The chief phytosterol present in the wheat grain is sitosterol. The embryo also contains sitosterol, but the phytosterol in the bran differs in its properties from sitosterol. The unsaponifiable ether extract of the vegetative organs, leaves, stems, etc., contains a phytosterol, together with an *alcohol*, $C_{20}H_{42}O$, crystallising from ethyl acetate and acetone in granular lumps of small crystals, m. p. 83°; *acetate*, m. p. 65°; it does not give the cholesterol colour reactions.

The amount of phytosterol in normal wheat plants is greater than that which was present in the grain from which the plants were grown; in etiolated plants, an increase in the phytosterol content as compared with the grain is not perceptible. It is suggested that the sterols form an essential part of cell membranes.

H. W. B.

Plant Sterols. II.. Occurrence of Phytosterol in some of the Lower Plants. MARY TAYLOR ELLIS (*Biochem. J.*, 1918, **12**, 173—177).—Ergosterol and fongisterol occur in the fungus *Polyporus nigricans*, and probably also in *P. betulinus.* Sterols may also be detected in *Laminaria, Sphagnum, Agaricus rubescens*, and *Lactarius subdulcis.* H. W. B.

Some Poisonous Plants in the Order Solanaceæ. II. Nicotiana suaveolens. J. M. PETRIE (*Proc. Linn. Soc. N.S. Wales*, 1916, **41**, 148—151; from *Physiol. Abstr.*, 1918, **3**, 199).— This plant contains nicotine. S. B. S.

The Production of Anthocyanins and Anthocyanidins. III. ARTHUR ERNEST EVEREST (*Proc. Roy. Soc.*, [B], **90**, 251—265. Compare A., 1914, i, 978; 1915, i, 25).—The author has isolated the anthocyanin pigment from the purplish-black viola, "Black Knight," petals, and has shown that it is a delphinidin glucoside and identical with the violanin obtained by Willstätter and Weil from the bluish-black pansy (compare *Annalen*, 1916, **412**, 178). An examination of the alum reaction as described by Willstätter and his collaborators shows that the colour reactions of anthocyanins, described as due to alum, are really due to the presence of iron as an impurity in the alum, and are not obtained if the reagent is pure.

An examination of the yellow sap pigment from the same violas shows that it ·contains a myricetin glucoside (or less probably a gossypetin glucoside) and also another yellow sap pigment which does not give a green coloration with dilute alkalis. Thus the presence in one flower of an anthocyanin pigment and of the flavonol derivatives from which it would be produced by reduction is shown for the first time. W. G.

Organic Chemistry.

Synthesis of αδη-Heptanetriol, True Homologue of Ordinary Glycerol, and of some Derivatives of Propyltetrahydrofuran. J. HAMONET (*Ann. Chim.*, 1918, [ix], **10,** 5—30).—In part a more detailed account of work already published (compare A., 1916, i, 246). When αη-dimethoxyheptan-δ-ol is acted on by phosphorus tri-iodide, it yields methyl iodide and 2-γ-*methoxypropyltetrahydrofuran*, b. p. 190—192°, D^{18} 0·9559, n_D^{19} 1·440, and not the required iododimethoxyheptane. Similar attempts to prepare the corresponding bromo-compound were not successful, but *δ-chloro-αη-dimethoxyheptane*, b. p. 120—122°/ 16 mm., was obtained by the action of phosphorus trichloride. αη-Dibromoheptan-δ-ol (*loc. cit.*), when distilled, decomposed, giving 2-γ-*bromopropyltetrahydrofuran*, b. p. 115—116°/27 mm., D^{20} 1·331, n_D^{20} 1·485.   W. G.

Preparation of certain Alkylating Reagents. JAMES COLQUHOUN IRVINE and WALTER NORMAN HAWORTH (Brit. Pat. 117824, 1918).—In the interaction of sulphuryl chloride and methyl or ethyl alcohol, the formation of an alkyl chlorosulphonate and alkyl sulphate have been observed (Behrend, A., 1877, i, 182; ii, 287), but under suitable conditions the main product is a mixture of alkyl sulphate and alkyl hydrogen sulphate. On distillation under diminished pressure, the alkyl hydrogen sulphate in the mixture undergoes decomposition into sulphuric acid and alkyl sulphate, so that a good yield of the latter is obtained. The sulphuryl chloride may be preformed or may be prepared in situ from sulphur dioxide and chlorine. [See also *J. Soc. Chem. Ind.*, 606A.]   D. F. T.

Kephalin. V. Hydrokephalin of the Egg-yolk. P. A. LEVENE and C. J. WEST (*J. Biol. Chem.*, 1918, **35,** 285—290. Compare this vol., i, 98).—Hydrokephalin has been isolated in an almost pure state from the sample of hydrolecithin previously suspected of containing it (*loc. cit.*). The raw material was freed from unsaturated compounds by dissolving in chloroform and then pouring into a large excess of ether. It was then subjected to repeated fractional crystallisation from a mixture of equal volumes of chloroform and ethyl methyl ketone, and then from a mixture of chloroform and alcohol (1:2). The final preparation had the correct empirical composition, $C_{41}H_{82}O_8NP$, corresponding with the structure $C_{17}H_{35} \cdot CO \cdot O \cdot CH \begin{cases} CH_2 \cdot O \cdot CO \cdot C_{17}H_{35} \\ CH_2 \cdot O \cdot PO(OH) \ O \cdot CH_2 \cdot CH_2 \cdot NH_2 \end{cases}$, which may therefore be regarded as established for the substance. The rotation of the pure substance is $[\alpha]_D^{20}$ in chloroform $+6 \cdot 0°$.
                                H. W. B.

Manufacture of Ethylidene Diacetate. Société Chimique des Usines du Rhône (Brit. Pat. 112766, 1918).—Ethylidene acetate is prepared by passing acetylene into a solution of mercuric oxide in glacial acetic acid to which an alkyl sulphate, particularly methylene sulphate, has also been added. [See also *J. Soc. Chem. Ind.*, 606A.] D. F. T.

The Acid Function in the Methenic and Methinic Derivatives. J. Guinchant (*Ann. Chim.*, 1918, [ix], **9**, 49—108; 109—143; 1918, [ix], **10**, 30—84).—A more detailed account of work already published (compare A., 1895, i, 649; 1896, i, 594; ii, 12, 465). W. G.

Reduction of Aldehydes to Corresponding Alcohols. I. Reduction of Heptaldehyde. P. A. Levene and F. A. Taylor (*J. Biol. Chem.*, 1918, **35**, 281—283).—The method is essentially the same as that employed for the reduction of esters (Levene and Allen, A., 1917, i, 3). An emulsion of metallic sodium in toluene is first prepared, and a solution of the aldehyde in glacial acetic acid and toluene is slowly added, the mixture being continuously cooled and stirred. The yield is about 60% of the theoretical. *Heptyl phenylcarbamate*, $C_{14}H_{21}O_2N$, prepared by heating the alcohol with an equal weight of phenylcarbimide at 175° for a few minutes, crystallises from dilute alcohol in needles, m. p. 60° (corr.). H. W. B.

Effect of Variations in the Available Alkali on the Yield of Acetone in the Oxidation of Butyric Acid with Hydrogen Peroxide. Edgar J. Witzemann (*J. Biol. Chem.*, 1918, **35**, 83—100).—When butyric acid is oxidised by means of hydrogen peroxide in dilute solution in the presence of variable amounts of alkali hydroxide, the quantity of acetone recoverable is greatest when the reaction of the system is neutral to faintly acid. As the alkalinity increases, the velocity of oxidation of the butyric acid also increases, but the yield of acetone decreases probably because the acetone itself becomes increasingly susceptible to oxidation with the increasing alkalinity. When dextrose is added to the reaction mixture, the products of oxidation of the dextrose reduce the alkalinity if the supply of alkali is limited, resulting in an increased production of acetone. If, however, there is an excess of alkali, the dextrose exerts a "sparing" action on the butyric acid which is analogous to the "sparing effect" of carbohydrate in the body. H. W. B.

*iso*Phorone. Maurice Delacre (*Bull. Soc. chim.*, 1918, [iv], **23**, 219—224. Compare A., 1911, i, 939, and following abstracts).—The author has prepared and purified, as far as possible, by distillation a large quantity of *iso*phorone, and from it has obtained two oximes, one having m. p. 70—73° and the other m. p. 97—100°. When boiled with alcoholic potassium hydroxide, the oxime, m. p. 73°, is slowly converted into its isomeride. Only one semicarbazone, m. p. 187°, was obtained. W. G.

Homophorone. MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 224—229. Compare A., 1911, i, 939, and preceding and succeeding abstracts).—From the fraction 160—200° obtained in the fractionation of crude *isophorone*, *homophorone*, $C_9H_{14}O$, has been isolated as a colourless liquid, b. p. 192—194°, giving only one *oxime*, m. p. 87—88°, which, unlike those from *isophorone*, is easily decomposed by hydrochloric acid, but is not transformed into an isomeride by potassium hydroxide. *Homophorone semi-carbazone* has m. p. 206°. W. G.

Action of Dilute Sulphuric Acid on Pure Pinacone. MAURICE DELACRE (*Bull. Soc. chim.*, 1918, [iv], **23**, 229—232. Compare preceding abstracts).—A theoretical discussion of work already published (compare A., 1911, i, 347, 939). W. G.

The Conversion of Lævulose-diphosphoric Acid into the Corresponding Monophosphoric Acid. CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 432—436).—This conversion can be brought about by gentle warming of a salt with N-hydrochloric acid or oxalic acid. The calcium salt of the monophosphoric acid has the formula $C_6H_{11}O_9PCa,H_2O$, and the barium salt $C_6H_{11}O_9PBa,H_2O$. The monophosphate can be fermented by living yeast, whereas the diphosphate cannot. S. B. S.

Oxidation Product of Creatine. LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918, **35**, 277—280).— After the removal of carnosine from an aqueous extract of muscle by means of mercuric acetate and sodium carbonate, a glistening, flaky substance is gradually precipitated from the filtrate. By decomposition of the precipitate with hydrogen sulphide and re-crystallisation from water, *a-methylguanidinoglyoxylic acid*,

$$NH_2 \cdot C(NH) \cdot NMe \cdot CO \cdot CO_2H, 2H_2O,$$
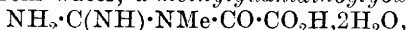
is obtained in the form of glistening flakes, m. p. 203—204°. The new compound is evidently produced from creatine by the oxidising action of mercuric acetate, and can also be prepared directly by the oxidation of either pure creatine or creatinine. It is somewhat toxic, 0·15 gram injected into a guinea-pig causing death in two hours. Its injection into a dog increases the elimination of creatine in the urine. H. W. B.

Hypochlorous, Hypobromous, and Hypoiodous Amides. ÉTIENNE BOISMENU (*Ann. Chim.*, 1918, [ix], **9**, 144—188).—A résumé of work already published (compare A., 1911, i, 957; 1912, i, 15, 97). W. G.

Action of the Chlorides of Phosphorus on Phenol-sulphonic Acids. II. RICHARD ANSCHÜTZ and EUGEN MOLINEUS (*Annalen*, 1918, **415**, 51—64. Compare A., 1908, i. 83). *p*-Chlorosulphonylphenyl dichloro-orthophosphate,

$$SO_2Cl \cdot C_6H_4 \cdot O \cdot POCl_2,$$
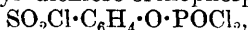
is converted by heating with an equimolecular quantity of phosphorus pentachloride at 180° into *p*-chlorophenyl dichloro-orthophosphate, and the latter, treated similarly at 250°, is converted quantitatively into *p*-dichlorobenzene.   p-*Chlorosulphonylphenyl metaphosphate*, $SO_2Cl \cdot C_6H_4 \cdot O \cdot PO_2$, obtained by heating the corresponding dichloride with the calculated quantity of water (weighed in the form of anhydrous oxalic acid), forms transparent crystals and is converted into *p*-chlorosulphonylphenyl dihydrogen phosphate by exposure to moisture in the air.

Potassium p-*acetoxybenzenesulphonate*, $SO_3K \cdot C_6H_4 \cdot OAc$, crystals, prepared by heating potassium phenol-*p*-sulphonate with acetic anhydride at 150°, is converted by phosphorus pentachloride on the water-bath into p-*acetoxybenzenesulphonyl chloride*, crystals, m. p. 78°, b. p. 148°/12 mm., which reacts in ethereal solution with aniline, *p*-toluidine, and piperidine (2 mols.) to form the *anilide*, $OAc \cdot C_6H_4 \cdot SO_2 \cdot NHPh$, m. p. 126—127°, p-*toluidide*, m. p. 98—99°, and *piperidide*, m. p. 115—116°, respectively. These three substances are converted by heating with alcohol (the first requires potassium hydroxide in addition) into *phenol*-p-*sulphonanilide*, needles, m. p. 137—138°, -p-*toluidide*, needles, m. p. 151—152°, and -*piperidide*, m. p. 132—133°, respectively.

When heated with carbon tetrachloride and phosphorus pentachloride at 180—200°, 2 : 6-dibromo-4-chlorosulphonylphenyl dichloro-orthophosphate (*loc. cit.*) is converted into 4-*chloro*-3 : 5-*dibromobenzenesulphonyl chloride*, $C_6H_2ClBr_2 \cdot SO_2Cl$, crystals, m. p. 94·5°, b. p. 203—208°, and this is converted into 1 : 2 : 4 : 6-tetrachlorobenzene by phosphorus pentachloride at 200°.   C. S.

Sulphonylides.   RICHARD ANSCHÜTZ (*Annalen*, 1918, **415,** 64—97.   Compare A., 1912, i, 852).—[With (FRL.) CLARA ZYMANDL.]—o-*Chlorosulphonylphenyl dichloro-orthophosphate*,
$$SO_2Cl \cdot C_6H_4 \cdot O \cdot POCl_2,$$
yellow oil, b. p. 185°, obtained from sodium phenol-*o*-sulphonate and phosphorus pentachloride (rather more than 1 mol.), is converted by heating with phosphorus pentachloride at 150° into o-*chlorophenyl dichloro-orthophosphate*, pale yellow oil, b. p. 135—137°/12 mm., which yields *o*-chlorophenol by boiling with water, and *o*-dichlorobenzene by heating with phosphorus pentachloride at 250°.
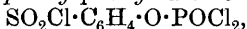
Sodium acetoxybenzene-o-*sulphonate*, $OAc \cdot C_6H_4 \cdot SO_3Na$, obtained by heating the phenol-*o*-sulphonate with acetic anhydride, is converted by phosphorus pentachloride into *acetoxybenzene*-o-*sulphonyl chloride*, colourless crystals, m. p. 73·2—73·9°, which yields the *sulphonanilide*, $OAc \cdot C_6H_4 \cdot SO_2 \cdot NHPh$, m. p. 106—107°, and *sulphon*-p-*toluidide*, leaflets, m. p. 116—117°, by treatment with aniline and *p*-toluidine respectively; these are hydrolysed, the latter by boiling alcohol alone, the former by the calculated quantity of boiling alcoholic potassium hydroxide, yielding *phenol*-o-*sulphonanilide*, $OH \cdot C_6H_4 \cdot SO_2 \cdot NHPh$, leaflets, m. p. 126·5—127·5°, and *phenol*-o-*sulphon*-p-*toluidide*, leaflets, m. p. 124—125°,

each of which develops a violet coloration with alcoholic ferric chloride. Phenylene-o-sulphonylide is produced when an ethereal solution of acetoxybenzene-o-sulphonyl chloride is treated with gaseous ammonia or with an ethereal solution of diethylamine, acetyl chloride being eliminated.

[With L. HODENIUS.]—*Sodium 4-acetoxytoluene-3-sulphonate*, prepared from the *p*-cresolsulphonate and acetic anhydride at 150°, is converted by phosphorus pentachloride into *4-acetoxytoluene-3-sulphonyl chloride*, m. p. 55—56°, b. p. 165—170°/20 mm., which yields tolylene-3:4-sulphonylide by treatment with ethereal ammonia or diethylamine. The following three compounds are prepared by methods similar to the preceding: *sodium 4-acetoxytoluene-3:5-disulphonate*, *4-acetoxytoluene-3:5-disulphonyl chloride*, crystals, m. p. 115°, and *4-acetoxytoluene-3:5-disulphonyldiethylamide*, $OAc \cdot C_6H_2Me(SO_2 \cdot NEt_2)_2$, crystals, m. p. 150°.

Tolylene-3:4-sulphonylide-5:5′-disulphonic acid,

$$SO_3H \cdot C_6H_2Me < ^{O \cdot SO_2}_{SO_2 \cdot O} > C_6H_2Me \cdot SO_3H, 3H_2O,$$
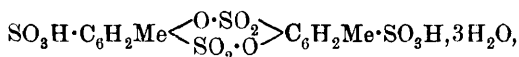
is prepared by treating *p*-cresol-3:5-disulphonic acid with fuming sulphuric acid (60% SO_3), finally at 100° with the further addition of the fuming acid, and recrystallising the precipitate from dilute nitric acid; it forms a *potassium* salt, long needles with $5\frac{1}{2}H_2O$, *silver* salt, colourless needles, and *ferric* salt, colourless needles, and, when anhydrous, reacts with phosphorus pentachloride to form *tolylene-3:4-sulphonylide-5:5′-disulphonyl chloride*, crystals, decomp. about 280°, which is stable to boiling water.

1:4-tert.-Butylphenol-3-sulphonic acid, $CMe_3 \cdot C_6H_3(OH) \cdot SO_3H$, is obtained by heating *p-tert.*-butylphenol with pure sulphuric acid at 70—80°. Its *sodium* salt, anhydrous crystals, yields by acetylation *sodium 4-acetoxy-1-tert.-butylbenzene-3-sulphonate*, which is converted by phosphorus pentachloride on the water-bath into *4-acetoxy-1-tert.-butylbenzene-3-sulphonyl chloride*, crystals, m. p. 103°. tert.-*Butylphenylene-3:4-sulphonylide*,

$$CMe_3 \cdot C_6H_3 < ^{O \cdot SO_2}_{SO_2 \cdot O} > C_6H_3 \cdot CMe_3,$$
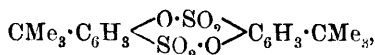
microscopic needles, m. p. 301—302°, is obtained by the action of phosphoryl chloride on 1:4-*tert.*-butylphenol-3-sulphonic acid. The following amyl compounds are prepared like the corresponding butyl compounds: *1:4-tert.-amylphenol-3-sulphonic acid* and its *sodium* salt, *sodium 4-acetoxy-1-tert.-amylbenzene-3-sulphonate*, *4-acetoxy-1-tert.-amylbenzene-3-sulphonyl chloride*, b. p. 142—146°/14 mm., and tert.-*amylphenylene-3:4-sulphonylide*, colourless crystals, m. p. 228—229°.

The substance obtained by Schiff (*Annalen*, 1875, **178**, 187) by treating sulphotannic acid or its acetyl derivative with acetic anhydride is *5:6-diacetoxy-o-phenylenesulphonylide*.

[With (FRL.) MARIA MAXIM.]—*Sodium 2-acetoxynaphthalene-1-sulphonate*, faintly red needles, prepared by acetylating the

naphtholsulphonate, is converted by phosphorus pentachloride in the presence of chloroform into 2-*acetoxynaphthalene*-1-*sulphonyl chloride*, crystals, m. p. 115·5°, which cannot be converted into a sulphonylide by means of pyridine, neither can 2-*naphthol*-1-*sulphonyl chloride*, colourless needles, m. p. 124°, obtained by hydrolysing the preceding acetyl derivative with warm dilute sodium hydroxide. The following derivatives of 1-naphthol-2-sulphonic acid are obtained by methods similar to the preceding: *potassium* 1-*acetoxynaphthalene*-2-*sulphonate*, colourless prisms, 1-*acetoxynaphthalene*-2-*sulphonyl chloride*, crystalline powder, m. p. 87·5°, 1-*acetoxynaphthalene*-2-*sulphonamide*, stout, yellow needles without a sharp m. p., and the corresponding *sulphonanilide*, $OAc \cdot C_{10}H_6 \cdot SO_2 \cdot NHPh$, crystals, m. p. 157·5°, and *sulphon*-p-*toluidide*, m. p. 135·5°. 2:1-*Naphthylenesulphonylide*,

$$C_{10}H_6 \diagdown \substack{O \cdot SO_2 \\ SO_2 \cdot O} \diagup C_{10}H_6,$$
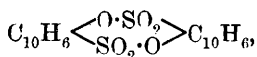
colourless, crystalline powder, decomp. above 300°, is obtained (1) by adding phosphoryl chloride with cooling to a mixture of potassium 1-naphthol-2-sulphonate, pyridine, and chloroform, (2) by shaking 1-acetoxynaphthalene-2-sulphonyl chloride with pyridine at the ordinary temperature.

Sodium 2-naphthol-1-sulphonate yields 2-naphthol-1:3:6:7-tetrasulphonic acid by heating with four parts of fuming sulphuric acid (40% SO_3) at 120—130° for eight hours, but when heated with five parts for two days is converted into a substance, colourless crystals, which appears to be 3:2-*naphthylenesulphonylide*-1:6:7:1′:6′:7′-*hexasulphonic acid* (*sodium* salt, $C_{20}H_6O_{24}S_8Na_6$, colourless, prismatic needles).

Acetylisethionyl chloride, $OAc \cdot CH_2 \cdot CH_2 \cdot SO_2Cl$, b. p. 130—132°/ 14 mm., obtained, together with β-chloroethylsulphonyl chloride by heating potassium acetylisethionate with phosphorus pentachloride on the water-bath, cannot be converted into diethylenesulphonylide by means of ammonia or diethylamine; the sulphonylide also cannot be prepared from isethionic acid and phosphoric oxide or phosphoryl chloride.   C. S.

The Stereochemistry of Quinquevalent Nitrogen. VI. SHIGERU KOMATSU (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 151—159).— After reviewing the state of knowledge with respect to the decomposition of quaternary ammonium compounds by heat and the various proposals for the representation of the spatial distribution of the valencies of the quinquevalent nitrogen atom, the author agrees with the assumption that four of the valencies possess the same value, whilst the fifth is of a different nature and suggests an extension of the views of Meisenheimer (A., 1909, i, 20; 1912, i, 25; 1913, i, 595) on the structure of the quinquevalent nitrogen atom. The atom is regarded as situate at the centre of a tetrahedron, at the corners of which the four radicles are disposed; the fifth and negative radicle is in an outer zone, and occupies a fixed

position which, however, may vary with the manner of formation of the ammonium compound, thus influencing the optical rotation of the substance, but leaving the chemical properties unaffected. By this hypothesis, the existence of two modifications of *d*-phenyl-benzylmethylallylammonium iodide (Komatsu, A., 19i5, i, 1054) is explained. D. F. T.

The Solidifying and Boiling Points of Phenol and the Cresols. J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1918, **37**, 268—272T).—The authors have determined the freezing-point and boiling-point curves of mixtures of phenol, and *o*-, *m*-, and *p*-cresols taken in pairs. Phenol and *o*-cresol show a continuous freezing-point curve with a minimum corresponding nearly with equimolecular proportions, but no eutectic point. The boiling-point curve is nearly a straight line. The phenol–*m*-cresol freezing-point curve has two minimum (eutectic) points, and between them a maximum at 17°, indicating the formation of a moleculai compound of the formula $C_6H_5 \cdot OH, 2C_7H_7 \cdot OH$. The compound forms a eutectic with phenol at 10·2° and with *m*-cresol at −4°. The boiling-point curve is a normal binary mixture curve. The freezing-point curve for phenol and *p*-cresol shows a sharp eutectic with equimolecular proportions of the constituents, whilst the boiling-point curve is normal.

When the cresols are taken in pairs, those containing *m*-cresol show the most complicated curves. The freezing-point curve of *m*- and *p*-cresols shows a maximum at 20% *p*-cresol, but only one eutectic, a 50% mixture, was detected. The curve for *o*- and *m*-cresols shows two distinct breaks, but no maximum, and the existence of a compound cannot be inferred.

The results show that many different mixtures of phenol and the cresols have the same freezing point. It is unsafe to consider a sample of "cresylic acid" free from phenol because it yields a distillate which does not freeze when immersed in ice-water. E. H. R.

Nitro-derivatives of Guaiacol. Fanny Pollecoff and Robert Robinson (T., 1918, **113**, 645—656).—The nitration of 4-nitroguaiacol yields 4:6-dinitroguaiacol, and of 4-nitroguaiacyl acetate a mixture of the 3:4- and the 4:5-dinitro-derivatives in undetermined proportions. By nitration, guaiacol carbonate yields successively 5-*nitro-2-methoxyphenyl carbonate*,

$$(NO_2 \cdot C_6H_3 \cdot OMe)_2CO_3,$$
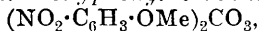
colourless needles, m. p. 133°, and 3:5-*dinitro-2-methoxyphenyl carbonate*, colourless needles, m. p. 148°, which yield on hydrolysis 5-nitroguaiacol and 3:5-*dinitroguaiacol*, pale yellow needles, m. p. 80°, respectively. The nitration of 5-nitroguaiacol yields 5:6-*dinitroguaiacol*, yellow prisms, m. p. 205—208° (decomp.) (*acetate*, colourless needles, m. p. 124—125°), together with the 4:5-isomeride as by-product; the former, aftei reduction and treatment with phenanthraquinone, yields 1-*hydroxy-2-methoxyphenanthra-*

phenazine, golden-yellow needles, m. p. 224°. 4 : 5-*Dinitroguaiacol*
forms pale yellow needles, m. p. 172° (*acetate,* colourless, pris-
matic needles, m. p. 123—124°, sintering at 114°), and is converted
as above into 2-*hydroxy*-3-*methoxyphenanthraphenazine*, yellow
threads, m. p. 239—240°.

The further nitration of 4 : 6-, 5 : 6-, or 4 : 5-dinitroguaiacol is
not practicable, but the 3 : 5-isomeride readily yields 3 : 5 : 6-*trinitro-
guaiacol,* yellow prisms, m. p. 129° (decomp.), as the sole product,
which forms a characteristic *pyridine* salt, $C_7H_5O_8N_3,C_5H_5N$, yellow
needles, m. p. 180°, 185°, or 194—195° (decomp.; according to the
rate of heating), and yields 3 : 5 : 6-*trinitroveratrole,* pale yellow
needles, m. p. 174°, by methylation. The last compound is con-
verted into 3 : 5-*dinitro*-2 : 6-*diaminoanisole,* garnet needles, m. p.
237°, by boiling methyl-alcoholic aqueous ammonia, and into
4 : 6-*dinitro*-1 : 2 : 3-*trimethoxybenzene,* pale yellow needles, m. p.
85°, by boiling methyl-alcoholic potassium hydroxide.   C. S.

Synthesis of Elemicin and of *iso*Elemicin. F. MAUTHNER
(*Annalen,* 1917, **414,** 250—255).—2 : 6-*Dimethoxyphenyl allyl
ether,* $C_6H_3(OMe)_2 \cdot O \cdot CH_2 \cdot CH:CH_2$, a colourless oil, b. p.
140—141°/14 mm., prepared from allyl bromide and pyrogallol
2 : 6-dimethyl ether in boiling acetone in the presence of potassium
carbonate, is converted by heating at 220° in a few minutes into
2 : 6-*dimethoxy*-4-*allylphenol,* $OH \cdot C_6H_2(OMe)_2 \cdot CH_2 \cdot CH:CH_2$, b. p.
168—169°/11 mm., which yields by methylation with methyl
sulphate and 10% sodium hydroxide solution 3 : 4 : 5-trimethoxy-
allylbenzene, identical with elemicin. The position of the allyl
group is proved by oxidising the substance in acetone to gallic acid
trimethyl ether by potassium permanganate, and of the double
linking by the decomposition of the ozonide by water, whereby
homogallaldehyde trimethyl ether is obtained. By heating with
alcoholic potassium hydroxide, the synthetic elemicin is converted
into *iso*elemicin (3 : 4 : 5-trimethoxypropenylbenzene), the ozonide of
which yields gallaldehyde trimethyl ether by decomposition with
water. [See *J. Soc. Chem. Ind.,* October.]   C. S.

**Synthesis by means of Sodamide. VIII. Phenyldi-
methylethyl Alcohol, Benzyl-, *o*-, *m*-, and *p*-Methylbenzyl- and
p-Methoxybenzyl-dimethylethyl Alcohols.** ALBIN HALLER and
EDOUARD BAUER (*Ann. Chim.,* 1918, [ix], **9,** 5—24).—A résumé of
work already published (compare A., 1911, i, 726; 1913. i, 168,
488; 1914, i, 418).   W. G.

**Terpenes and Ethereal Oils. CXXI. Pulegenic Acid
and the Conversion of Carvone into Pulegenic Acid.** O.
WALLACH (*Annalen,* 1917, **414,** 233—243).—An improved method
of preparing pulegenic acid is to shake pulegone dibromide with
aqueous potassium hydroxide for one hour at the ordinary tempera-
ture, and then for three hours at 100°. Unchanged pulegone and
methyl*cyclo*hexanone are removed by steam, and pulegenic acid is

extracted by ether from the somewhat concentrated, acidified residual solution.

Like other substances containing a semicyclic linking, pulegenic

acid, $CMe_2:C\underset{CH_2\text{------}CH_2}{\overset{CH(CO_2H)\cdot CHMe}{<}}$ (and also its amide), is difficult

to reduce to the saturated acid, which, however, can be obtained as follows: hydrogen chloride is added on to methyl pulegenate, and then removed again with simultaneous hydrolysis. The product is a mixture of ordinary pulegenic acid and an isomeride. By distillation under ordinary pressure, the former is converted into pulegene, whilst the latter distils at 256—260° with slight decomposition. It is converted into its amide, m. p. 152°, which is reduced easily by hydrogen and colloidal palladium to dihydropulegenamide, m. p. 150—151° (Eykman gives 147°), from which dihydropulegenic (1-methyl-3-isopropyl*cyclo*pentane-2-carboxylic) acid, b. p. 139°/12 mm., D^{24} 0·9600, n_D 1·4524, is readily obtained. An alternative and more convenient method is to heat methyl hydrochloropulegenate with aniline, to reduce the resulting unsaturated ester by Skita's method, and to hydrolyse the product.

Dihydropulegenamide is converted by Hofmann's method into a *base*, presumably 2-*amino*-1-*methyl*-3-iso*propyl*cyclo*pentane*, which forms an *acetyl* derivative, $C_{11}H_{21}ON$, m. p. 132°, and a *carbamide*, $C_{10}H_{20}ON_2$, m. p. 190°.

[With WOLFGANG VON RECHENBERG.]—The conversion of the 6-ring in carvone into the 5-ring of pulegenic acid, and the formation of this acid from dihydrocarvenolic acid, have been effected as follows. Dihydrocarvenolide, prepared from *d*-carvone, is hydrolysed by potassium hydroxide and boiling amyl alcohol, and the resulting dihydrocarvenolic acid, m. p. 87°, is converted by methyl-alcoholic hydrogen chloride at 0° into a saturated, chlorinated ester, m. p. 15—16°, b. p. 114°/12 mm., which yields pulegenic acid, b. p. 142—145°/11 mm., D^{20} 0·9975, n_D 1·4747, $[\alpha]_D^{20} + 32\cdot67°$ in ether, by boiling with alcoholic sodium methoxide and subsequent hydrolysis. The pulegenic acid thus obtained is converted into its amide, m. p. 152° (occasionally 123°; conditions of formation unknown), which yields dihydropulegenamide, m. p. 150—151°, by reduction as above. C. S.

Total Synthesis of α-Fenchenylanic Acid (*alloapo*-**Camphanecarboxylic Acid**), **and a New Type of Decomposition of Ozonides.** GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennicae*, *A.*, [x], **18**, 1—7; from *Chem. Zentr.*, 1918, i, 623—624).—In the ozonisation of α-fenchene (Komppa and

CH
CH₂   CH₂
| CMe₂ |
CH₂   CH·CO₂H
CH

(I.)

CH
CH₂   CH₂
| CMe₂ |
CH₂   CH·OH
CH

(II.)

x^*
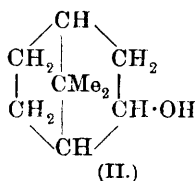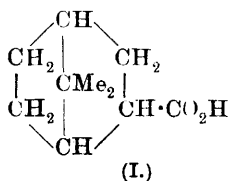
Hintikka, A., 1914, i, 557; Komppa and Roschier, A., 1917, i, 466), the authors have obtained α-fenchocamphorone and fenchenylanic acid (annexed formula, I). The constitution of the latter is now confirmed by a synthesis of the acid from dl-α-fenchocamphorone, which, on reduction with sodium and alcohol, yields dl-α-*fenchocamphorol* (annexed formula, II), needles, m. p. 122—124°, b. p. 203°; from this, by conversion into the corresponding dl-α-*fenchocamphoryl chloride*, $C_9H_{15}Cl$, m. p. approx. 24—25°, b. p. 74·5°/ 13 mm., an organo-magnesium compound is obtainable which reacts with carbon dioxide, with formation of dl-α-fenchenylanic acid (*alloa*pocamphanecarboxylic acid). This result proves that the decomposition of the ozonide of α-fenchene does not entirely follow the normal course, but that to some extent decomposition occurs without scission of a carbon atom, possibly as indicated by the scheme:

$$>C<^{CH_2 \cdot O}_{O—O} \rightarrow >C<^{CH_2}_{O—}>O \rightarrow$$

$$>CH \cdot CH<^O_O \rightarrow >CH \cdot CO_2H.$$
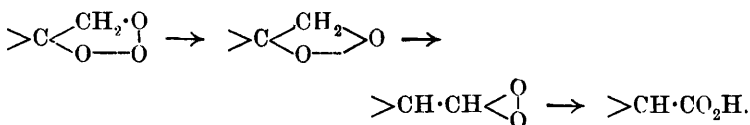
D. F. T.

Action of Nitrous Acid on Methyl p-Dimethylaminobenzoate and p-Dimethylaminobenzaldehyde. (Reactions of *tert.*-Amines, and a Contribution to the Subject of Steric Hindrance). FRANZ KLAUS and OSKAR BAUDISCH (*Ber.*, 1918, **51**, 1036—1048. Compare A., 1907, i, 131).—When methyl p-dimethylaminobenzoate is treated with sodium nitrite and hydrochloric acid at −5°, it yields methyl 3-nitro-4-dimethylaminobenzoate, m. p. 75° (Reverdin and Delétra, A., 1906, i, 273), and *methyl p-nitrosomethylaminobenzoate*, $CO_2Me \cdot C_6H_4 \cdot NMe \cdot NO$, which crystallises in satiny needles, m. p. 115·5°. The identity of the latter compound is established by its reactions (A) and synthesis (B). A.—It yields p-nitrosomethylaminobenzoic acid, m. p. 202°, on hydrolysis with sodium hydroxide; it gives p-methylaminobenzoic acid, m. p. 163°, and its methyl ester, m. p. 95·5° (not 73—75°, as Johnston stated, P., 1905, 156), when boiled with aqueous and methyl-alcoholic hydrochloric acid, respectively. B.—Methyl p-methylaminobenzoate is prepared by esterifying the acid or by hydrolysing p-nitrosomethylaminobenzoic acid with methyl-alcoholic hydrogen chloride, and is treated with nitrous acid, or methyl anthranilate is methylated by means of methyl sulphate and then nitrosated.

p-Dimethylaminobenzaldehyde behaves in a similar manner towards nitrous acid, the products being p-*nitrosomethylaminobenzaldehyde*, $CHO \cdot C_6H_4 \cdot NMe \cdot NO$, pale straw-yellow crystals, m. p. 78°, 3-nitro-4-dimethylaminobenzaldehyde, m. p. 105°, and p-nitrosodimethylaniline. J. C. W.

Amino-oxides. OSKAR BAUDISCH (*Ber.*, 1918, **51**, 1048—1058) —The action of permonosulphuric acid on p-dimethylaminobenzoic

acid leads to the formation of the sulphate of an amino-oxide. The free amino-oxide can be obtained by precipitation with potassium acetate, and it is found to give a number of characteristic salts, presumably of the oxonium type, and to behave in an interesting manner towards nitrous and sulphurous acids.

p-*Dimethylaminobenzoic acid* N-*oxide*, $CO_2H \cdot C_6H_4 \cdot NMe_2 \dot{:} O$, crystallises in very long, prismatic needles, m. p. $192 \cdot 5°$, gives formaldehyde when heated, and yields the following salts: *sulphate*, feathery groups of needles, as much as an inch long, with $1H_2O$, m. p. $160°$ (decomp.); *hydrochloride*, snow-white needles, m. p. $184°$; *aurichloride*, reddish-yellow, m. p. $136°$; *picrate*, yellow needles, m. p. $155°$; *platinichloride*, pink needles, m. p. 155—$156°$; *ferrocyanide*, white needles. When a solution of the sulphate is saturated with sulphur dioxide, it suddenly becomes green and deposits white crystals of 4-*dimethylamino*-3-*sulphobenzoic acid*, $CO_2H \cdot C_6H_3(NMe_2) \cdot SO_3H$, m. p. 279—$280°$, the mother liquor containing p-dimethylaminobenzoic acid. A solution in dilute hydrochloric acid, when treated with sodium nitrite, yields some p-nitrodimethylaniline, a trace of p-nitrosodimethylaniline, but chiefly 3-nitro-4-dimethylaminobenzoic acid (A., 1907, i, 132). This has been reduced by means of stannous chloride to 3-*amino*-4-*dimethylaminobenzoic acid*, which crystallises in pale pink leaflets, m. p. 152—$153°$, and forms a *hydrochloride*, long needles, m. p. $237°$, solutions of which give a deep red coloration and crystalline precipitate when warmed with ferric chloride.

p-*Diethylaminobenzoic acid* N-*oxide* has been prepared in a similar manner. It crystallises in long needles, m. p. 170—$171°$, evolves acetaldehyde on heating, and yields the following salts: *sulphate*, $1H_2O$, long, white needles, m. p. $173 \cdot 5$—$174 \cdot 5°$; *hydrochloride*, m. p. $162 \cdot 5$—$163 \cdot 5°$; *platinichloride*, m. p. $178°$; *aurichloride*, m. p. $177°$; *picrate*, m. p. 169—$171°$; and *hydrogen ferrocyanide*, snowy leaflets. Sulphurous acid reduces it to p-diethylaminobenzoic acid and 4-*diethylamino*-3-*sulphobenzoic acid*, m. p. 308—$310°$, and nitrous acid converts it into a mixture of p-nitrosoethylaniline, p-nitrosoethylaminobenzoic acid, 3-nitro-4-ethylaminobenzoic acid, 3-nitro-4-diethylaminobenzoic acid, and p-nitrodiethylaniline. J. C. W.

*iso*Valeric Acid, and its Abnormal Behaviour in the Perkin Synthesis. ALFRED SCHAARSCHMIDT, E. GEORGEACOPOL and JOHANN HERZENBERG (*Ber.*, 1918, **51**, 1059—1074).—When *iso*valeric acid is applied to aldehydes under the conditions of the Perkin reaction, the main products are not the expected unsaturated acids, but the ethylenes derived from these by loss of carbon dioxide. The condensations take place at unusually low temperatures, so low, in fact, that it is doubtful if the unsaturated acids represent an intermediate stage at all. The authors believe that the primary α-hydroxy-acid first loses carbon dioxide and then water rather than suffer decomposition in the reverse order.

The results of the experiments described are summarised as

follows, the weights, in grams, being given in brackets: Benz-aldehyde (15), *iso*valeric anhydride (50), sodium *iso*valerate (45), heated for thirty hours at 100°, gave α-*iso*propylcinnamic acid, CHPh:CPr$^\beta$·CO$_2$H (1·9), leaflets, m. p. 118·5°, and α-phenyl-γ-methyl-Δ$^\alpha$-butene, CHPh:CHPr$^\beta$ (9·3). The same reagents, in the proportions 50:175:150, heated for six hours at 150°, gave the same hydrocarbon (46) (Schramm, A., 1883, 1094; Kunckell, A., 1904, i, 386; Klages, *ibid.*, 569). Benzaldehyde (15), acetic anhydride (55), and sodium *iso*valerate (45), heated for thirty hours at 100°, gave the same hydrocarbon (0·6), but no acid. Benzaldehyde (15), *iso*valeric anhydride (55), and sodium acetate (45), heated for ten hours at 150°, gave the hydrocarbon (3·2) and ordinary cinnamic acid (11).

Furfuraldehyde (50), *iso*valeric anhydride (150), and sodium *iso*valerate, heated for five hours at 150°, gave α-2-*furyl*-γ-*methyl*-Δ$^\alpha$-*butene*, C$_4$H$_3$O·CH:CHPr$^\beta$ (32), a pleasant-smelling, pale yellow oil, b. p. 64—66°/13 mm., 165—167°/atm., and a trace of β-2-*furyl*-α-*iso*propylacrylic acid, C$_4$H$_3$O·CH:CPr$^\beta$·CO$_2$H (0·5), colourless leaflets, m. p. 114°. Furfuraldehyde (25), acetic anhydride (250), and sodium *iso*valerate (75), heated for seven hours at 150°, gave no hydrocarbon, but 6 grams of β-2-furylacrylic acid, m. p. 140°.

Anisaldehyde (50), *iso*valeric anhydride (175), and sodium *iso*valerate (150), heated for eight hours at 150°, gave α-*p*-methoxy-phenyl-γ-methyl-Δ$^\alpha$-butene (22) (Moureu and Chauvet, A., 1897, i, 404) and p-*methoxy*-α-*iso*propylcinnamic acid,

$$\text{OMe·C}_6\text{H}_4\text{·CH:CPr}^\beta\text{·CO}_2\text{H},$$
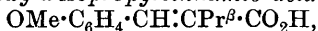
needles, m. p. 134—135°.

No definite results were obtained with *o*-nitrobenzaldehyde, salicylaldehyde, cinnamaldehyde, or *iso*butaldehyde. The aliphatic aldehyde gave no hydrocarbon or acid, whilst the others reacted very sluggishly.   J. C. W.

The Double Acid from Normal and *allo*-**Cinnamic Acids.** A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1230—1233).—The double acid can be prepared (1) by crystal-lisation from a solution saturated with respect to both acids, and (2) by exposing a dilute solution of sodium cinnamate (about 1%) to light for several months, evaporating to dryness, acidifying the residue with hydrochloric acid, and extracting the organic acids with hot light petroleum; the cold extract ultimately yields crystals of the double acid. A saturated solution of the two acids in equilibrium with the *allo*-acid of m. p. 42°, inoculated with the *allo*-acid of m. p. 58° or 68°, soon crystallises, and solutions are obtained which are in equilibrium with these two modifications. If these solutions are allowed to evaporate, the double acid separates, together with the modification of the *allo*-acid used for inoculation. The double acids obtained from these solutions consist of 50% of normal acid and 50% of *allo*-acid, all melt in the same way, sintering at about 56° and being completely molten

at about 90°, and are all proved to be identical in the following way. An aqueous solution saturated with the normal acid and the *allo*-acid at the ordinary temperature, and in equilibrium with the *allo*-acid of m. p. 42°, was prepared, and to portions of this solution crystals of the double acids were added. They produced no effect whatever. Had the various double acids been different, that produced in the presence of *allo*-acid of m. p. 58° (or 68°) should have brought about crystallisation of the *allo*-acid of m. p. 58° (or 68°) and of the corresponding double acid.

The identity of the various double acids supports Biilmann's view that the three modifications of *allo*-cinnamic acid are trimorphous, and is opposed to Stobbe and Schönburg's theory that they are three different chemical individuals. C. S.

α-Naphthoicsulphinide. KURT KALCHER (*Annalen*, 1917, **414,** 244—249).—α-Cyanonaphthalene-β-sulphonyl chloride, m. p. 143—144° (Friedländer and Woroshzow, A., 1912, i, 293, give 141—142°), is converted by ammonia gas in hot, dry benzene solution into *α-cyanonaphthalene-β-sulphonamide*, monoclinic crystals, decomp. 300—340°, which is converted by boiling $N/10$-sodium hydroxide ($1\frac{1}{4}$ mols.) and subsequent acidification into *α-naphthoicsulphinide*, $C_{10}H_6 \!\!<^{CO}_{SO_2}\!\!> NH$, clusters of small prisms, m. p. 244°, together with the sodium salt of an acidic by-product. The sulphinide, which is best purified through its *sodium* salt, long, flattened needles, has a bitter taste and forms a *methyl* derivative, leaflets, m. p. 220—221°, which yields methylamine by hydrolysis with 35% hydrochloric acid at 150°. The nature of the acidic by-product has not been established. C. S.

A New Benzanthrone Synthesis. II. Transformation of 1-Phenylnaphthalene-2 : 3-dicarboxylic Anhydride into Benzanthronecarboxylic Acid. ALFRED SCHAARSCHMIDT and ERNST KORTEN (*Ber.*, 1918, **51**, 1074—1082. Compare A., 1917, i, 274).—1-Phenylnaphthalene-2 : 3-dicarboxylic anhydride (I) was first converted into 3 : 4-benzofluorenone-1-carboxylic acid (II) by prolonged treatment with concentrated sulphuric acid at the ordinary temperature (Stobbe, A., 1907, i, 766), and recently by means of aluminium chloride in benzene (A., 1916, i, 47). In order to hasten the older process, the authors have tried the effect of heating the anhydride with 91% sulphuric acid at 155°, the mixture being stirred for three hours. Under these conditions, two different products are obtained, namely, benzanthronecarboxylic acid, III (*loc. cit.*), which is insoluble in boiling water, and a soluble, red *sulphonic acid*, $C_{18}H_{10}O_6S$. This has the structure of a fluorenone, for it yields an oxime, and since it is non-fluorescent in sulphuric acid, it is most probably a derivative of 3 : 4-benzofluorenone-1-carboxylic acid. The same products are obtained by

treating this acid in the above manner, and the chief reaction can therefore be represented thus:

$$CO \qquad \qquad CO_2H \qquad \qquad CO_2H$$

(I.) $\qquad\qquad$ (II.) $\qquad\qquad$ (III.)
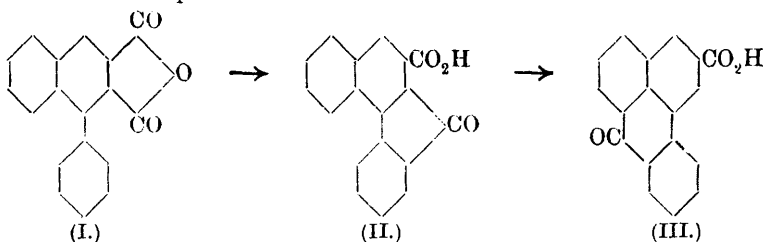
It illustrates the rupture of a weak five-membered ring and the establishment of a six-membered system. A similar change is suffered by 3:4-benzofluorenone itself when heated with sulphuric acid, for fluorescence is developed, but in this case the chief effect is sulphonation.

The imide of the original acid exhibits the same phenomenon most readily. 1-*Phenylnaphthalene*-2:3-*dicarbimide*, m. p. 249°, is obtained by heating the anhydride with ammonia at 240—250°. When warmed with 96% sulphuric acid at 75° for five minutes, this yields 3:4-benzofluorenone-1-carboxylic acid and its orange-red *amide*, m. p. 281—282°, whilst at 130°, *benzanthronecarboxamide*, m. p. 306°, is formed. This has been prepared from the acid (III) for comparison, and it exhibits a brilliant yellowish-green fluorescence in sulphuric acid. J. C. W.

A New Benzanthrone Synthesis. III. ALFRED SCHAARSCHMIDT and E. GEORGEACOPOL (*Ber.*, 1918, **51**, 1082—1087. Compare A., 1917, i, 274).—As already suggested, experiments prove that when 3:4-benzofluorenone is fused with potassium hydroxide, it yields the salts of 1-phenylnaphthalene-2-carboxylic acid and o-α-*naphthylbenzoic acid*. The free acids may be separated by means of methyl alcohol, from which the latter acid, being only moderately soluble, crystallises in colourless rhombohedra, m. p. 161·5°. If the acids are treated with phosphorus pentachloride and then aluminium chloride, the former yields 3:4-benzofluorenone again, whilst the latter gives benzanthrone. This ketone may also be prepared by the distillation of the ammonium salt of its carboxylic acid. J. C. W.

Oxidation of Santonin by means of Organic Per-acids. GUIDO CUSMANO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 117—121; *Gazzetta*, 1918, **48**, i, 248—253).—Oxidation of santonin by means of perbenzoic or peracetic acid results in the formation of two products: (1) *iso*Artemisin or δ-oxysantonin. (2) ε-*Oxysantonin*, $C_{15}H_{18}O_4$, which crystallises in bundles of acicular prisms, m. p. 154°, at which temperature it is stable; it does not react with phenylcarbimide, and yields only a *monophenylhydrazone*,

$$C_{15}H_{18}O_3:N_2HPh,$$
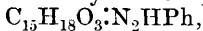
m. p. about 280°. ε-Oxysantonin is not altered by aqueous alkali

hydroxide, but the lactone ring of its molecule may be opened by means of hot alcoholic sodium ethoxide, which changes the colour to blood-red with a transitory green fluorescence; the *acid*, $C_{15}H_{20}O_5$, thus obtained forms crystals, m. p. about 100°, and when heated with dilute sulphuric acid gives the original oxysantonin.

Treatment of ε-oxysantonin with concentrated hydrochloric acid in the cold yields a new *chlorosantonin*, $C_{15}H_{17}O_3Cl$, which forms crystals, m. p. about 196°, and is transformed into ε-oxysantonin by either cold alcoholic potassium hydroxide or boiling aqueous alcohol; by zinc dust and a few drops of acetic acid in alcoholic solution, it is converted into santonin.   T. H. P.

o-2′ : 4′-**Dihydroxybenzoyltetrachlorobenzoic Acid and 2 : 3 : 4-Trichloro-6-hydroxyxanthone-1-carboxylic Acid and some of their Derivatives.** W. R. ORNDORFF and W. A. ADAMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1235—1256).—After surveying the results of the numerous investigations on *o*-dihydroxybenzoylbenzoic acid (Baeyer's monoresorcinphthalein, *Annalen*, 1876, **183**, 23), the authors describe in detail the preparation of *o*-2′ : 4′-dihydroxybenzoyltetrachlorobenzoic acid from resorcinol and tetrachlorophthalic acid or its anhydride. Tetrachlorofluorescein is always formed, and some unchanged tetrachlorophthalic acid always remains, whatever the experimental conditions. The best results are obtained by heating resorcinol (4 parts) and tetrachlorophthalic acid (5 parts) for twelve to fifteen hours at a temperature not exceeding 131° (vapour of boiling xylene), whereby *o*-2′ : 4′-dihydroxybenzoyltetrachlorobenzoic acid is obtained in a yield of about 90%. The substance, after purification through its acetate, forms colourless crystals containing $2H_2O$, and has m. p. 227°, with decomposition into tetrachlorofluorescein and tetrachlorophthalic anhydride. It forms a *triacetate*, $C_{14}H_3O_5Cl_4Ac_3$, colourless crystals, m. p. 166—167°, a *sodium* salt,
$$C_{14}H_5O_5Cl_4Na,2H_2O,$$
slightly grey crystals, m. p. about 295° (decomp.), *hydroxylammonium* salt, $C_{14}H_6O_5Cl_4,NH_2 \cdot OH$, pale yellow crystals, m. p. 254° (decomp.; darkening at 230°), and with dry ammonia an unstable *triammonium* salt and a stable *monoammonium* salt. By bromination in glacial acetic acid, it yields o-3′ : 5′-*dibromo*-2′ : 4′-*dihydroxybenzoyltetrachlorobenzoic* acid, yellow needles, m. p. 211—212°, which at this temperature is converted into tetrachlorophthalic anhydride and tetrachloroeosin. The dibromo-acid forms a *triacetate*, colourless crystals, m. p. 204·5°, and an unstable, yellow *tetra-ammonium* salt, and a stable, less highly coloured *diammonium* salt.
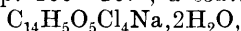
By treatment for several hours with 5% alcoholic potassium hydroxide and subsequent acidification, the triacetate of the unbrominated acid yields 2 : 3 : 4-*trichloro*-6-*hydroxyxanthone*-1-*carboxylic acid*, colourless needles containing $2H_2O$. m. p. 279—280° (anhydrous). The same substance is obtained by boiling the dihydroxybenzoyltetrachlorobenzoic acid with 5% aqueous sodium hydroxide. It forms a *disodium* salt, $C_{14}H_3O_5Cl_3Na_2$, yellow

needles, *monoacetate*, colourless needles or prisms, decomp. 220—221°, and *ammonium* salt, $C_{14}H_4O_5Cl_3(NH_4)$.

The preceding results, particularly the fact that the triacetates are stable compounds which do not undergo any change when boiled with alcohol, are interpreted by ascribing to *o*-2′:4′-dihydroxy-benzoyltetrachlorobenzoic acid the constitution

$$O<\begin{matrix} ----C(OH) \cdot C_6H_3(OH)_2 \\ CO \cdot C_6Cl_4 \end{matrix}.$$
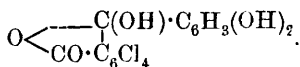
It seems highly probable from the results of this investigation that the formation of phthaleins takes place in two steps. First, an additive product of the phenol and the anhydride analogous to the preceding dihydroxy-acid is formed, and then this reacts with a second molecule of the phenol with the loss of water to form the phthalein.   C. S.

Constitution of Phthalyl- and Succinyl-malonic Esters. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, **51**, 1106—1115).—Two alternative formulæ for ethyl phthalylmalonate have been advocated, (I) by Wislicenus (A., 1888, 149) and (II) by Scheiber (A., 1912, i, 559):

$$\begin{matrix} C_6H_4 \cdot C{:}C(CO_2Et)_2 \\ CO ---O \end{matrix} \qquad\qquad C_6H_4<\begin{matrix} CO \\ CO \end{matrix}>C(CO_2Et)_2$$

(I.)   (II.)
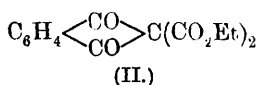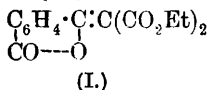
If formula II is correct, the ester should correspond in optical properties with indandiones, but this is not the case. A compound of the type I, on the other hand, should resemble ethyl benzylidene-malonate (A., 1911, ii, 782), when due allowance is made for the influence of the lactone ring. It is now found that these esters are optically related, like *a*-phenyl-Δ^a-propylene and ethylidene-phthalide, CHPh:CHMe and $\begin{matrix} C_6H_4 \cdot C{:}CHMe \\ CO—O \end{matrix}$, and consequently ethyl phthalylmalonate is correctly represented by formula I. This can be harmonised with the view that phthalyl chloride is symmetrical in structure, for the reaction with ethyl sodiomalonate can include stages which may be represented thus:

$$C_6H_4<\begin{matrix} CO \cdot CH(CO_2Et)_2 \\ COCl \end{matrix} \rightarrow C_6H_4<\begin{matrix} C{:}C(CO_2Et)_2 \\ OH \\ COCl \end{matrix} \rightarrow$$

$$C_6H_4<\begin{matrix} C{:}C(CO_2Et)_2 \\ >O \\ CO \end{matrix}$$
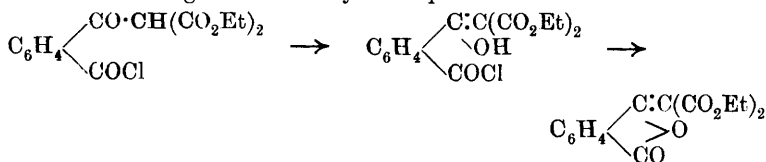
Similarly, ethyl succinylmalonate is abnormal in optical properties, and must therefore be expressed by formula III rather than by Scheiber's formula IV (A., 1909, i, 363):

$$\begin{matrix} CH_2 \cdot CH_2 \cdot C{:}C(CO_2Et)_2 \\ CO ----O \end{matrix} \qquad\qquad \begin{matrix} CH_2 \cdot CO \\ CH_2 \cdot CO \end{matrix}>C(CO_2Et)_2$$

(III.)   (IV.)
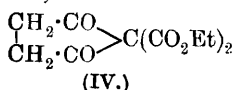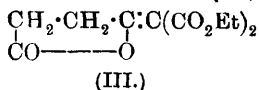
Ethyl phthalylmalonate (I) has m. p. 74 – 75°, $D_4^{84\cdot4}$ 1·1887, n_a 1·53416. n_D 1·54105, n_β 1·56155. at 84·4°, $E\Sigma_a$ 2·13, $E\Sigma_D$ 2·25, $E\Sigma_\beta - \Sigma_a$ 122%. 2 : 2-Diethylindan-1 : 3-dione (Freund and Fleischer, A., 1910, i. 490) has b. p. 157—159°/15 mm., $D_4^{14\cdot5}$ 1·0693, n_a 1·53658, n_D 1·54174, n_β 1·55632, n_γ 1·56967, at 14·5°, $E\Sigma_a$ 1·43, $E\Sigma_D$ 1·49, $E\Sigma_\beta - \Sigma_a$ 54%, $E\Sigma_\gamma - \Sigma_a$ 57%. 4 : 7-Dimethyl-2 : 2-diethylindan-1 : 3-dione (Freund and Fleischer, A., 1916, i, 317) has b. p. 153°/12 mm., m. p. 51 – 52°, $D_4^{62\cdot4}$ 1·0174, n_a 1·52107, n_D 1·52598, n_β 1·54051, at 62·4°, $E\Sigma_a$ 1·56, $E\Sigma_D$ 1·63, $E\Sigma_\beta - \Sigma_a$ 63%. Ethyl succinylmalonate (III) has m. p. 68°, D_4^{73} 1·1675, n_a 1·46923, n_D 1·47245, n_β 1·48170, n_γ 1·48952, at 73°, $E\Sigma_a$ 1·13, $E\Sigma_D$ 1·15, $E\Sigma_\beta - \Sigma_a$ 41%, $E\Sigma_\gamma - \Sigma_a$ 42%. Ethylidenephthalide has b. p. 152°/11 mm., m. p. 64°, $D_4^{99\cdot4}$ 1·1053, n_a 1·56394, n_D 1·57054, at 99·4, $E\Sigma_a$ 2·29, $E\Sigma_D$ 2·36, and a-phenyl-Δ^a-propylene has $E\Sigma_a$ 1·09, $E\Sigma_D$ 1·19.   J. C. W.

N- and *O*-Methyl Ethers of Ketoximes. The Four Isomeric Methyl Ethers of Phenyl *p*-Tolyl Ketoxime. LEOPOLD SEMPER and LEO LICHTENSTADT (*Ber.*, 1918, **51**, 928—942).—The *N*- and *O*-methyl ethers of ketoximes are produced in approximately equal quantities by the action of methyl sulphate on aqueous alcoholic alkaline solutions of the oximes. Thus, benzophenoneoxime yields the *N*-methyl ether, long needles, m. p. 102—103°, *hydrochloride*, m. p. 140—143°, and *O*-methyl ether, stout crystals, m. p. 60—61°. These are separated as follows: the initial product, after extraction with ether in the usual way, is triturated with light petroleum, b. p. 30—50°, which leaves most of the *N*-ether, this being recrystallised from a petroleum of b. p. 60—70°; the solution is treated with hydrogen chloride gas, which precipitates the remaining *N*-ether as hydrochloride, and then the *O*-ether is recovered by evaporation and crystallised from alcohol. The *N*-ether exhibits a tendency to form crystalline additive compounds, of which the following are some examples: with benzophenoneoxime, 1 : 1, cubes, m. p. 108—109° (compare Alessandri, A., 1915, i, 412); a *demihydrate*, transparent leaflets, m. p. 78—80°; a *compound* with quinol, 2 : 1, m. p. 186—186·5°; a *compound* with phenylcarbimide, 1 : 1, m. p. 141—142°. These are highly dissociated in solution. The *O*-ether forms no such compounds.

These preliminary experiments with a simple ketoxime paved the way for an attempt to isolate the two stereoisomeric pairs of ethers from an unsymmetrical ketoxime. For the purpose of investigation, phenyl *p*-tolyl ketone was chosen. A better method for isolating the α- and β-oximes of this has been devised (compare Hantzsch, A., 1890, 1273), and each isomeride converted into its *N*- and *O*-methyl ethers, making, therefore, the four possible isomerides.

The crude phenyl *p*-tolyl ketoxime is resolved into the two isomerides by crystallisation from 90% alcohol, which deposits most of the α-oxime on cooling, the β-oxime being recovered by adding to the hot mother liquor about three-fifths of its bulk of hot water, and cooling. The oximes are further purified by crystallisation

from pure alcohol. The α-oxime forms long, slender needles, m. p. 153—154°; the β-oxime crystallises in stout, transparent prisms, m. p. 136·5—137·5°. These are methylated as above, and the crude products treated in the same way. The two *N*-ethers have such tendencies to form additive compounds, however, that the products which are found to be sparingly soluble in the volatile petroleum are not the free ethers, but compounds with the un-methylated oximes. These are decomposed by dissolving them in dilute aqueous-alcoholic sodium hydroxide, precipitating the oxime by means of dilute sulphuric acid, and extracting the ethers after neutralisation of the filtrate. The α-N-*methyl ether* (I) forms colourless tablets, m. p. 91—92°, and yields the following *additive compounds*: with 0·5H₂O, transparent, rhombic tablets, m. p. 66—67·5°; with α-phenyl *p*-tolyl ketoxime, needles, m. p. 106—107°; with the β-oxime, short prisms, m. p. 90—92°. The α-O-*methyl ether* (II) crystallises in needles, m. p. 64—68°.

$$\begin{array}{cccc}
\text{C}_7\text{H}_7\cdot\overset{\displaystyle||}{\text{C}}\text{Ph} & \text{C}_7\text{H}_7\cdot\overset{\displaystyle||}{\text{C}}\text{Ph} & \text{C}_7\text{H}_7\cdot\overset{\displaystyle||}{\text{C}}\text{Ph} & \text{C}_7\text{H}_7\cdot\overset{\displaystyle||}{\text{C}}\text{Ph} \\
\text{Me}\cdot\text{N:O} & \text{N}\cdot\text{OMe} & \text{O:NMe} & \text{MeO}\cdot\text{N} \\
\text{(I.)} & \text{(II.)} & \text{(III.)} & \text{(IV.)}
\end{array}$$
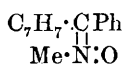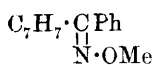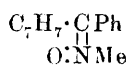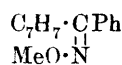
The β-N-*methyl ether* (III) forms long, glistening prisms, m. p. 113—114°, and yields *additive compounds* with the β-oxime (stout prisms, m. p. 81—82°) and α-oxime (small cubes, m. p. 124—125°). The β-O-*methyl ether* (IV) has b. p. 184—185°/16 mm., 135—136°/ 0·5 mm. The two *N*-ethers are hydrolysed by boiling hydrochloric acid to phenyl *p*-tolyl ketone and β-methylhydroxylamine hydrochloride, and reduced by zinc dust and acetic acid to a base which may be isolated as a *hydrochloride*, C₁₅H₁₆NCl, m. p. 199—201°.

J. C. W.

Synthesis of some Phenolic Ketones. Taste of the Ketones.

HIROSHI NOMURA and FUSATOSHI NOZAWA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 79—92).—Vanillin and piperonal possess pleasant odours, whereas zingerone (methyl 4-hydroxy-3-methoxyphenylethyl-ketone) and the analogous 3:4-methylenedioxyphenylethyl methyl ketone have a pungent taste, but the intermediate products in the synthesis of these substances from vanillin and piperonal, namely, 4-hydroxy-3-methoxystyryl methyl ketone and 3:4-methylenedi-oxystyryl methyl ketone, are almost tasteless when first brought into contact with the tongue, although they gradually develop pungency. A number of compounds of similar constitution have now been examined with a view to discover the influence of constitutional variations on the taste. As in the above case of 4-hydroxy-3-methoxystyryl methyl ketone, the primary condensation product is generally less readily soluble than its final reduction product in organic solvents, and does not immediately taste pungent, whereas the reduction products are markedly pungent; styryl methyl ketone is exceptional in being readily soluble and having a very tingling taste. The presence of a free phenolic group is not essential to pungency, because phenylethyl methyl ketone, *p*-methoxyphenyl-

ethyl methyl ketone, and 3:4-methylenedioxyphenylethyl methyl ketone are all pungent. The degree of pungency, however, is greatly influenced by the position of the free hydroxyl group with respect to the ketonic side-chain; o-hydroxyphenylethyl methyl ketone in taste resembles 2-hydroxy-3-methoxyphenylethyl methyl ketone, and p-hydroxyphenylethyl methyl ketone resembles zingerone. As in these cases the hydroxyphenylethyl methyl ketones are less pungent than the corresponding hydroxymethoxyphenylethyl methyl ketones, the m-methoxyl group appears to increase the pungency. The influence of the simple hydrocarbon radicle attached to the ketonic group is not much greater than that of the position of the hydroxyl group, because phenyl 4-hydroxy-3-methoxyphenylethyl ketone has a pungent taste similar to zingerone.

Most of the compounds examined have been described earlier. m-*Hydroxyphenylethyl methyl ketone*, $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot COMe$, m. p. 85—86°, was prepared through m-*hydroxystyryl methyl ketone*, needles, m. p. 97—98°, b. p. 208—209°/14 mm., from m-hydroxybenzaldehyde and acetone, the condensation of these substances being effected in a 10% solution of sodium hydroxide. p-*Hydroxyphenylethyl methyl ketone*, needles, m. p. 82—83°, was obtained by the catalytic reduction of p-hydroxystyryl methyl ketone in ethereal solution. The condensation of 2-hydroxy-3-methoxybenzaldehyde and acetone in alkaline solution yields 2-*hydroxy-3-methoxystyryl methyl ketone*,

$$OMe \cdot C_6H_3(OH) \cdot CH \text{\textrm{:}} CH \cdot COMe,$$
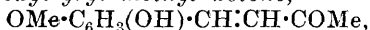
yellow crystals with $1H_2O$, m. p. 81—82°, or m. p. 77—77·5° if anhydrous, the catalytic reduction of which produces 2-*hydroxy-3-methoxyphenylethyl methyl ketone*, b. p. 206—207°/35 mm.; the pungent taste of this substance is accompanied by a paralysing effect, which is also observed with o-hydroxyphenylethyl methyl ketone. Vanillin and acetophenone undergo condensation in alkaline solution with the formation of *phenyl 4-hydroxy-3-methoxystyryl ketone*, $OMe \cdot C_6H_3(OH) \cdot CH \text{\textrm{:}} CH \cdot COPh$, yellow crystals, m. p. 92—93°, accompanied by *vanillylidenediacetophenone*,

$$OMe \cdot C_6H_3(OH) \cdot CH(CH_2 \cdot COPh)_2,$$
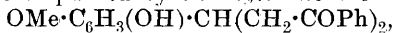
colourless crystals, m. p. 131—132° (*benzoyl* derivative, colourless, m. p. 133°); on reduction in the usual way, phenyl 4-hydroxy-3-methoxystyryl ketone gave *phenyl 4-hydroxy-3-methoxyphenylethyl ketone*, $OMe \cdot C_6H_3(OH) \cdot CH_2 \cdot CH_2 \cdot COPh$, colourless scales, m. p. 97·5—98°.   D. F. T.

Terpenes and Ethereal Oils. CXXII. Behaviour of the Nitrosochloride Additive Compounds towards Reagents which eliminate Hydrogen Chloride. O. WALLACH (*Annalen*, 1918, **414**, 257—270).—Sodium alkyloxides, anhydrous sodium acetate in glacial acetic acid, and dimethylaniline have been used to eliminate the elements of hydrogen chloride from nitrosochlorides, but each reagent has its disadvantages. The author now finds that an excellent conversion of a nitrosochloride into an oxime

is obtained by the use of a mixture of acetone and pyridine at not too high a temperature. Thus limonene nitrosochloride is converted into carvoxime by heating with acetone and pyridine for ten to fifteen minutes on the water-bath. In the case of certain nitroso-chlorides, hydrogen chloride is eliminated in different ways by different reagents.

[With JOHANNA WOLFF.]—α-Terpineol nitrosochloride is converted into 8-hydroxy-Δ^6-menthene-2-oneoxime by heating with acetone and pyridine on the water-bath, but when heated with anhydrous sodium acetate and glacial acetic acid, it yields a crystalline substance, $C_{10}H_{17}O_2N$, m. p. 139°, which is saturated, yields the keto-lactone of homoterpenylic acid by treatment with mineral acids, and is identical with the substance obtained by Cusmano and Linari from the hydroxylamino-oxime (A., 1912, i, 272); it is regarded as the oxime–oxide,

$$\mathrm{CMe}{<}\!\!\begin{array}{c}\mathrm{C(:NOH){\cdot}CH_2}\\ \mathrm{CH_2\text{-}\!\!\text{---}\!\!CH_2}\end{array}\!\!{>}\mathrm{CH{\cdot}CMe_2.}$$
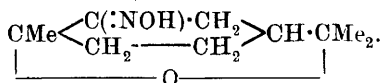
[With MARGARETE WALTER.]—β-Terpineol nitrosochloride does not yield a well-characterised product when treated with sodium methoxide (A., 1906, i, 372), and even when halogen acid is removed by the acetone–pyridine method, the expected hydroxy-oxime is only obtained by distillation in a vacuum as a slightly coloured, glassy mass.

The crystalline product, obtained by the prolonged action (about fourteen days) of 90% alcohol on β-terpineol nitrosochloride at the ordinary temperature and recrystallised from methyl alcohol, is not the hydroxy-oxime containing 1MeOH (Goodwin, *Diss.*, Göttingen, 1907), because it is a saturated substance, neither is it an oxime–oxide (see above), as is shown by the analytical data. Evidence is brought forward which indicates that the substance is a mixture, the halogen of the nitrosochloride being replaced partly by methoxyl, partly by ethoxyl, and partly by hydroxyl groups. Whether methyl or ethyl alcohol is used to decompose the nitroso-chloride and for the recrystallisation of the product, the saturated, crystalline substances all yield the same compound after hydrolysis by sulphuric or oxalic acid, namely, the ketone, $C_{10}H_{14}O$ (semi-carbazone, m. p. 218°), obtained by the hydrolysis by sulphuric acid of the unsaturated hydroxy-oxime resulting from the action of sodium methoxide (*loc. cit.*) or of pyridine on β-terpineol nitroso-chloride. By reduction with sodium and alcohol, the ketone, which is also produced in bad yield by boiling the nitrosochloride with dilute sulphuric acid (1:4), yields an *alcohol*, $C_{10}H_{16}O$, b. p. 108—112°/20 mm. (*phenylurethane*, m. p. 144°). C. S.

Terpenes and Ethereal Oils. CXXIII. Behaviour of Dibrominated Hexacyclic Ketones in Relation to the Position of the Bromine Atoms. O. WALLACH (*Annalen*, 1918, **414**, 271—296).—The conversion of dibrominated *cyclo*-hexanones into phenols is, of course, well known, and recently (A.,

1916, i, 213) unsaturated hydroaromatic tertiary alcohols have been converted into benzene hydrocarbons through the dibromo-additive compounds, but cases analogous to the smooth conversion of the 6-ring dibromopulegone into the 5-ring pulegenic acid under the action of alkali have hitherto not been known. The author has therefore examined the behaviour of a number of dibromo-derivatives of menthone and of carvomenthone when digested with 2% aqueous potassium hydroxide at the ordinary temperature for two to three days, and finds that the course of the reaction is determined essentially by the positions of the bromine atoms. The results may be generalised as follows: (1) Phenols are formed from dibromo-derivatives which have been obtained by the addition of bromine at an ethylenic linking adjacent to the carbonyl group and not separated from it by a substituent; for example, 1 : 2-dibromomenthone and 3 : 4-dibromocarvomenthone. The formation of the phenol does not always take place smoothly, comparatively stable monobromides sometimes being formed. (2) When the ethylenic linking is adjacent to the carbonyl group, but is separated from it by a substituent, the dibromo-derivative, for example, 4 : 5-dibromomenthone and 1 : 6-dibromocarvomenthone, readily undergoes fission of the ring with the production of an aliphatic ketonic acid with the same number of carbon atoms. (3) When the two bromine atoms are divided between the nucleus and the side-chains, or are both in the side-chains, the course of the reaction may be very varied and a general rule cannot be formulated. (4) Dibromo-derivatives in which the bromine atoms are attached to nuclear carbon atoms on either side of the carbonyl group, for example, 2 : 4-dibromomenthone and 1 : 3-dibromocarvomenthone, are converted into pentacyclic hydroxycarboxylic acids (see following abstract).

[With H. E. WOODMAN.]—When shaken for three days with 2% aqueous potassium hydroxide, 8 : 9-dibromomenthan-2-one, prepared by the bromination of optically active dihydrocarvone, is converted, apart from small quantities of carvacrol and carvenone, into a heavy oil, which loses hydrogen bromide and yields carvacrol when distilled in a vacuum, and is reduced to dihydrocarvone by zinc and aqueous sodium hydroxide, and is therefore probably the monobromide, $CHBr{:}CMe{\cdot}CH{<}^{CH_2{\cdot}CH_2}_{CH_2{-}CO}{>}CHMe$.

The crystalline dihydrocarvone dibromide, m. p. 69—70°, obtained by brominating l-dihydrocarvone in glacial acetic acid containing hydrogen bromide, is converted by 2% aqueous potassium hydroxide into an unsaturated *hydroxy-ketone*, $C_{10}H_{16}O_2$, b. p. 140°/16 mm., D^{20} 1·0285, n_D 1·4917 (*semicarbazone*, m. p. 123—124°), which yields carvacrol by warming with dilute sulphuric acid, and is possibly 8-hydroxy-Δ^6-menthen-2-one or 8-hydroxy-Δ^3-menthen-2-one.

3 : 4-Dibromocarvomenthone is converted by 2% aqueous potassium hydroxide into carvacrol, and, similarly, 1 : 2-dibromomenthone into *m*-cresol.

[With H. E. WOODMAN and W. JESSEN.]—1 : 6-Dibromocarvo-menthone is converted by shaking with 2% aqueous potassium hydroxide for two to three hours at the ordinary temperature, and then for one to two hours at 100° into ε-keto-β-*iso*propylheptoic acid, which is identified as the optically active modification by the formation of the semicarbazone, m. p. 158—159°, and the oxime, m. p. 60—63° (rising to 87—89° by recrystallisation).

[With ADOLF HALLSTEIN.]—When 1 : 2-dibromomenthone is shaken for sixteen to twenty hours with the quantity of 2% aqueous potassium hydroxide calculated to remove all the bromine, a *mono-bromide*, $C_{10}H_{15}OBr$, m. p. 42—43°, is obtained, together with some thymol. The monobromide is converted into thymol by heating it alone, when hydrogen bromide is evolved, or with sodium methoxide. This behaviour and the method of preparation indicate that the monobromide is 2-bromo-Δ^6-menthen-3-one or 2-bromo-Δ^1-menthen-3-one, but the substance does not react readily with bromine, and yields by oxidation with alkaline potassium permanganate oxalic acid, volatile fatty acids, and a *ketonic acid*, $C_{10}H_{14}O_3$, m. p. 105—106° (*silver* salt, $C_{10}H_{13}O_3Ag$; *semicarbazone*, m. p. 225°); the formation of the last acid is not explicable by either of the formulæ given above.

[With EMMA GROTE.]—4 : 5-Dibromomenthone is converted by 2% potassium hydroxide into an aliphatic *ketonic acid*, $C_{10}H_{18}O_3$ (*silver* salt, $C_{10}H_{17}O_3Ag$; *semicarbazone*, m. p. 161—163° [slowly heated] or 164—166° [rapidly heated]), which is probably ε-keto-βζ-*dimethyloctoic acid*, $COPr^\beta \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CO_2H$.

An unsatisfactory attempt to prepare $\Delta^{4(5)}$-menthen-3-one from 4-bromomenthan-3-one is described.   C. S.

Terpenes and Ethereal Oils. CXXIV. Method of Transforming Hexacyclic Ketones into *cyclo*Pentanones Based on the Conversion of Dibrominated *cyclo*Hexanones into Pentacyclic α-Hydroxy-carboxylic Acids. O. WALLACH [with MATHILDE GERHARDT and WILHELM JESSEN] (*Annalen*, 1918, **414**, 296—366).—A portion of the work has already appeared (A., 1916, i, 487).

The dibrominated *cyclo*hexanones which contain the bromine atoms in such positions that pentacyclic α-hydroxy-carboxylic acids are produced by the action of alkalis (see preceding abstract) are in general easily obtained by treating the *cyclo*hexanone in glacial acetic acid solution with four atoms of bromine. Since *cyclo*pentanones are known only in small number, whilst *cyclo*hexanones can be obtained in large numbers, not only from natural sources, but also from phenols by Sabatier's method and by Knoevenagel's synthesis, it is of importance to find out whether it is possible quite generally to convert *cyclo*hexanones into pentacyclic α-hydroxy-carboxylic acids with the same number of carbon atoms, from which *cyclo*pentanones can be obtained by oxidation. Up to the present time, nine *cyclo*hexanones have been converted into *cyclo*pentanones by the elimination of a nuclear methylene group, the penta-

cyclic α-hydroxy-carboxylic acids being intermediate products. The formation of these would be easily explicable if the original dibromo*cyclo*hexanone contained a CBr_2 group adjacent to the carbonyl group, because the alkali would then produce an ortho-diketone, from which the pentacyclic α-hydroxy-carboxylic acid would be formed by a benzilic acid transformation. This simple explanation is inapplicable, for two reasons: (1) It is proved quite definitely that by direct substitution in menthone and carvomenthone, the two bromine atoms are not attached to one and the same carbon atom, but that one bromine atom replaces the tertiary hydrogen atom adjacent to the carbonyl group and the other enters the methylene group on the other side of the carbonyl group. (2) Although compounds having the composition of *o*-diketones can be isolated, they do not exhibit the properties of such substances, but behave as unsaturated ketols. Such compounds derived from the dibromomenthone and the dibromocarvomenthone are identical and yield the same pentacyclic hydroxy-carboxylic acid. The author's explanation is represented schematically: for dibromomenthone,
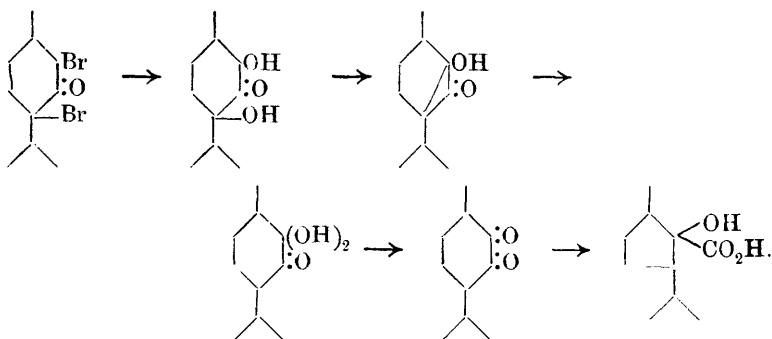
and similarly for the dibromocarvomenthone; the same *o*-diketone is formed in both cases, but when isolated isomerises to the unsaturated ketol,
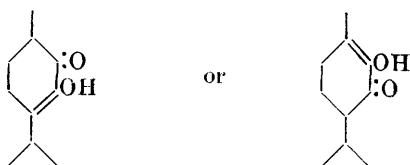
The bromination of 1 : 3-dimethyl*cyclo*hexan-5-one in cold glacial acetic acid produces two dibromo-compounds, an *α-dibromide*, $C_8H_{12}OBr_2$, needles, m. p. 163—164° (decomp.), which is scarcely attacked by alkali, and an isomeric *β-dibromide*, prisms, m. p. 60—61°, which is converted by 2% aqueous potassium hydroxide into the *ketol*, $C_8H_{12}O_2$, m. p. 71—72°. The ketol, which is removed from the acidified liquid by steam, is converted by con-

centrated aqueous potassium hydroxide at 140° into *4-hydroxy*-1 : 3-*dimethylcyclopentane-4-carboxylic acid*, $C_8H_{14}O_3$, colourless crystals, m. p. 92—93°, which yields 1 : 3-*dimethylcyclopentan-4-one*, b. p. 152—154°, D^{17} 0·8950, n_D^{17} 1·4330 (*semicarbazone*, m. p. 165—166°), by warming with lead peroxide and sulphuric acid.   C. S.

Terpenes and Ethereal Oils. CXXV. Compounds of the Eucarvone Series. O. Wallach [with Max Standacher], (*Annalen*, 1918, **414**, 367—375).—Assuming the constitution given to β-dihydroeucarvoxime (*Annalen*, 1914, **403**, 87) to be correct, the reduction of the substance should yield tetrahydroeucarvylamine. This is found to be so. When reduced by sodium and alcohol, the oxime is converted into a *base*, $C_{10}H_{19}\cdot NH_2$, b. p. 208·5°, D^{21} 0·8680, n_D 1·4665, which forms a *carbamide*, m. p. 139°, *phenylcarbamide*, m. p. 143—146°, *trimethylammonium iodide*, m. p. about 200°, and an *acetyl* derivative, m. p. 110·5°, the last being identical with the substance obtained by acetylating the base prepared by the reduction of tetrahydroeucarvoxime.

By bromination in glacial acetic acid at 0°, tetrahydroeucarvone yields a *monobromo*-derivative, $C_{10}H_{17}OBr$, crystals, m. p. 32°, which is converted by 3% aqueous potassium hydroxide into *hydroxytetrahydroeucarvone*, $OH\cdot C_{10}H_{17}O$, b. p. 98°/12·5 mm., D^{20} 0·9810, n_D 1·4626 (*semicarbazone*, m. p. 193°; *oxime*, m. p. 84°, which forms a crystalline *sodium* salt). The hydroxy-compound is reduced to a *glycol*, $C_{10}H_{18}(OH)_2$, b. p. 112—117°/4 mm., by sodium and alcohol, and yields a *chromate*, $(C_{10}H_{17}O)_2CrO_4$, when treated with sulphuric acid and chromium trioxide dissolved in a little water, at a temperature not exceeding 0°.

When treated with bromine (2 mols.) in glacial acetic acid without cooling, tetrahydroeucarvone yields *dibromotetrahydroeucarvone*, $C_{10}H_{16}OBr_2$, colourless prisms, m. p. 68°, which is converted by 4% aqueous potassium hydroxide at 100° into an *acid*, $C_{10}H_{16}O_2$, crystals, m. p. 91·5—92·5° (*silver* salt, $C_{10}H_{15}O_2Ag$). The acid is saturated, odourless, and somewhat easily volatile with steam; its constitution has not yet been determined. When treated with methyl-alcoholic sodium methoxide, dibromotetrahydroeucarvone yields a *substance*, $C_{10}H_{16}O_2$, b. p. 218—219°, D^{20} 0·979, n_D 1·4698, isomeric with the preceding acid, the nature of which has not yet been ascertained.   C. S.

Isomerisation Product of Carvone in the Light. Carvonecamphor. II. E. Sernagiotto (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 238—242. Compare A., 1915, i, 425).—When the oxime of carvonecamphor is heated with 20% sulphuric acid on the water-bath, *iso*carvonecamphor is obtained, the yield being almost theoretical. Phosphorus pentachloride reacts with the oxime in chloroform solution, giving 2-chlorocymene. From these and other reactions previously described, the annexed constitution is suggested for carvonecamphor.   R. V. S.

The Partial Synthesis of β- and γ-Fenchene. GUST. KOMPPA and R. H. ROSCHIER (*Ann. Acad. Sci. Fennicae*, 1917, *A*, [x], **15**, 1—15; from *Chem. Zentr.*, 1918, i, 622. Compare A., 1917, i, 398, 466).—In extension of the earlier conversion of *dl-α-*fenchocamphorone into α-fenchene, the authors have treated *dl-β-*fenchocamphorone with magnesium methyl iodide, with production of *methyl-β-fenchocamphorol* (annexed formula, I), prisms, m. p.
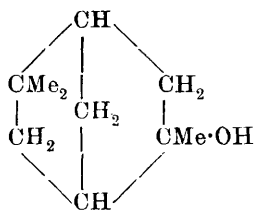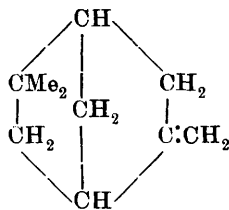
(I.)   (II.)
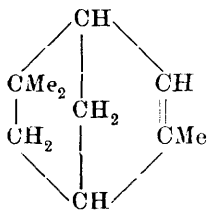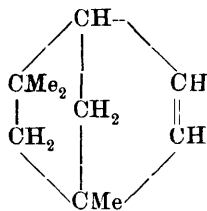
(III.)   (IV.)

66—67°, b. p. 77°/9 mm., 85°/15 mm.; *phenylurethane* derivative, $C_{17}H_{23}O_2N$, obtained by the action of phenylcarbimide, needles, m. p. 133·5—134°; *acetyl* derivative, $C_{12}H_{20}O_2$, b. p. 212·5°/766 mm., 80·5—81°/8 mm., D_4^{20} 0·9769, n_D^{20} 1·45884. When heated with potassium hydrogen sulphate, methyl-β-fenchocamphorol yields a mixture of hydrocarbons consisting mainly of dl-β-*fenchene* (formula II), b. p. 151—153°, D_4^{20} 0·8596, n_D^{20} 1·46581, with an endocyclic γ-fenchene (formula III), b. p. 146—148°, D_4^{20} 0·8539 n_D^{20} 1·46063, identical with the product of the interaction of *dl-*fenchyl alcohol and potassium hydrogen sulphate; *dl-*β-fenchene on oxidation with potassium permanganate gives dl-*hydroxy-β-fenchenic* acid, needles, m. p. 124—125° (*acetyl* derivative, $C_{12}H_{18}O_4$, scales, m. p. 117—118°); the acid is oxidised by lead dioxide and sulphuric acid to *dl-*β-fenchocamphorone, and this further by potassium permanganate to *apo*fenchocamphoric acid. The endocyclic fenchene (formula IV) described earlier (Roschier, *Diss.*, Helsinki, 1917), and termed *isoallo*fenchene by Semmler and *iso*fenchylene by Qvist, should be designated δ- or *iso-*fenchene. The compound now described by the authors as β-fenchene has been earlier termed *iso*fenchene by Semmler and *Dd-* (or *Ll-*) fenchene by Wallach.   D. F. T.

Terpenes and Ethereal Oils. CXX. O. WALLACH (*Annalen*, 1917, **414**, 195—233).—Most of the work has been already published (A., 1916, i, 213). The following is new.

[With KURT PELIKAN.]—From the accepted formulæ of pinol hydrate and dihydrocarveol, the expectation is justifiable that the reduction product of the former will be identical with the menthane-2:8-diol obtained from the latter by the addition of water (Wallach, *Annalen*, 1911, **380**, 161). The expectation, however, is not fulfilled. *i*-Pinol hydrate yields by reduction a glycol, dihydropinol hydrate, m. p. 139—141°, whilst the *i*-glycol obtained from dihydrocarveol has m. p. 108—109°. Also, *d*-pinol hydrate (sobrerol) reduced in methyl-alcoholic solution by Paal's method yields a *glycol*, $C_{10}H_{18}(OH)_2$, m. p. 158—159°, $[a]_D^{20°}$ − 40°26′ in alcohol, whilst the glycol derived from the optically active dihydrocarveol has m. p. 113—114°.

The behaviour of pinol hydrate on reduction, therefore, has been examined. When it is reduced by hydrogen and colloidal palladium in the absence of free acid, there occurs, in addition to the normal reduction, a by-reaction in which the pinol hydrate is dehydrated and the resulting unsaturated monohydric alcohol is reduced to tetrahydrocarveol. This result not only again shows that unsaturated glycols are not always smoothly reduced to the saturated glycols in the presence of colloidal metal (compare A., 1912, i, 878), but is also a further proof that in pinol hydrate a hydroxyl group occurs in position 2.

i- or *l*-Dihydropinol hydrate is converted into terpinene dihydrobromide by treatment with hydrogen bromide in glacial acetic acid. A similar transformation is not produced by hydrogen chloride. Moreover, the menthane-2:8-diol obtained from dihydrocarveol does not behave in this way.

It is shown that dihydropinol hydrate is not identical with menthane-1:4-diol or with *menthane-2:4-diol*, obtained by reducing sabinene glycol by Paal's method. The latter diol has b. p. 135—140°/9 mm.; the distillate solidifies completely (m. p. 93—94°), but separates as an oil from solvents on account of its great solubility. When dehydrated by oxalic acid and water, it yields a small quantity of a hydrocarbon, b. p. 172—182°, D^{20} 0·866, showing the reactions of terpinene, the main product being an unsaturated *alcohol*, $C_{10}H_{17}·OH$, b. p. 219—221°, D^{22} 0·9250. n_D 1·4790, which yields carvenone by oxidation with chromic acid and tetrahydrocarveol by reduction by Paal's method. The alcohol would therefore appear to be Δ^3-*menthene-2-ol*, but that $\Delta^{4(8)}$-menthene-2-ol is also present is indicated by the formation of acetone when the alcohol is oxidised by potassium permanganate. When *i*-dihydropinol hydrate is warmed with oxalic acid and water, the main product is a saturated *oxide* having an odour of cineole; dihydrocarveol is formed as a by-product.   C. S.

The Pungent Principles of Ginger. II. HIROSHI NOMURA (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 67—77. Compare T., 1917, **111**, 769).—By distillation of the pungent principles of Japanese ginger under reduced pressure, the author has been able to isolate,

in addition to zingerone, a substance, *shogaol*, $C_{17}H_{24}O_3$, b. p. 175—185°/0·4—0·5 mm., 231—238°/15·5 mm., M.W. in benzene 262, D_4^{25} 1·0448, n_D^{25} 1·52467; this substance is phenolic (*acetyl* derivative, b. p. 183—188°/0·6 mm.; *methyl* ether, b. p. 160—165°/ 0·06 mm.; *ethyl* ether, b. p. 181—186°/0·65 mm.), and also contains a methoxy-group; the third oxygen atom is probably ketonic. Oxidation of the ethyl ether with alkaline permanganate yields ethylvanillic acid, so that the constitution of shogaol may be represented $OH \cdot C \overset{C(OMe) \vdots CH}{\underset{CH———CH}{\big\langle}} C \cdot C_{10}H_{17}O$. From the facts that on reduction in ethereal solution with hydrogen and platinum-black shogaol yields *dihydroshogaol*, $C_{17}H_{26}O_3$, b. p. 166—169°/0·15 mm., and that the molecular refraction of shogaol greatly exceeds the calculated value, it appears probable that shogaol is a β-unsaturated ketone. D. F. T.

Some Derivatives of the Pyrryl Methyl Ketones with Furfuraldehyde. C. FINZI and E. VECCHI (*Gazzetta*, 1917, **47**, ii, 10—19).—Whereas benzaldehyde reacts equally easily with the 2- and 3-acetyl derivatives of pyrrole, the results now described show that furfuraldehyde reacts well and almost quantitatively with acetyl groups in the 2-position, but that the reaction with a 3-acetyl group appears to be influenced by the presence of some substituent group in the pyrrole nucleus. In view of their analogy to cinnamyl derivatives, the compounds obtained by the condensation of furfuraldehyde with the acetylpyrroles are termed *furacryl* derivatives.

The *compound*, $\overset{CH \cdot CH}{\underset{CH \cdot NH}{\big\rangle}} C \cdot CO \cdot CH \vdots CH \cdot C_4H_3O$, obtained by the interaction of 2-acetylpyrrole and furfuraldehyde, forms slightly iridescent, yellow needles, m. p. 134—135°.

The *compound*, $\overset{CH \cdot CMe}{\underset{CMe \cdot NH}{\big\rangle}} C \cdot CO \cdot CH \vdots CH \cdot C_4H_3O$, obtained from 2-acetyl-3:5-dimethylpyrrole and furfuraldehyde, forms sulphur-yellow needles, m. p. 181—182°.

The *compound*, $C_4HNMe_2(CO_2Et) \cdot CO \cdot CH \vdots CH \cdot C_4H_3O$, formed from ethyl 2-acetyl-3:5-dimethylpyrrole-4-carboxylate and furfuraldehyde, crystallises in lemon-yellow, prismatic needles, m. p. 184—185°. The corresponding *acid*,

$C_4HNMe_2(CO_2H) \cdot CO \cdot CH \vdots CH \cdot C_4H_3O$,

obtained either by hydrolysing this ester or by starting from the pyrrolecarboxylic acid, forms minute, yellow, prismatic crystals, m. p. 287—288°; the insoluble *silver* salt was analysed.

The *compound*, $\overset{CO_2Et \cdot C = CMe}{\underset{NH \cdot CMe}{\big\rangle}} C \cdot CO \cdot CH \vdots CH \cdot C_4H_3O$, obtained from ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate and furfuraldehyde, forms sulphur-yellow needles, m. p. 149—150°. The corresponding *acid* forms minute, straw-yellow, prismatic needles, m. p. 179—180° (decomp.); the corresponding *silver* salt was analysed.

The *compound*, $\begin{array}{c}\text{CH:C(CO·CH:CH·C}_4\text{H}_3\text{O)}\\ \text{CH:C(CO·CH:CH·C}_4\text{H}_3\text{O)}\end{array}{>}\text{NH}$, obtained from 2 : 5-diacetylpyrrole and furfuraldehyde, forms lemon-yellow crystals, m. p. 238—240°, and dissolves in concentrated sulphuric acid in the cold, giving an intense blue coloration with a violet border; dilution of this solution results in the precipitation of the unaltered compound. The corresponding dicinnamyl derivative is very slightly soluble in cold concentrated sulphuric acid, and only in the hot dissolves somewhat, giving a reddish-violet coloration.

The *compound*, $\begin{array}{c}\text{CAc·CMe}\\ \text{CMe–NH}\end{array}{>}\text{C·CO·CH:CH·C}_4\text{H}_3\text{O}$, formed from 2 : 4-diacetyl-3 : 5-dimethylpyrrole and furfuraldehyde, crystallises in tufts of prismatic needles, m. p. 170°, and dissolves in concentrated sulphuric acid, giving a carmine coloration, changing later to amaranth; on dilution, this solution deposits the original compound. The corresponding dicinnamyl derivative dissolves only slightly and slowly in cold concentrated sulphuric acid, giving the orange-yellow coloration shown with all the furacryl and cinnamyl derivatives of the pyrroles as yet examined.   T. H. P.

New Synthesis of Tetraphenylpyrrole. GERTRUDE MAUD ROBINSON and ROBERT ROBINSON (T., 1918, 113, 639—645).— Adopting a hypothesis, represented by the following scheme, to account for the conversion of phenylhydrazones into indoles, $\text{NHPh·N:CMe}_2 \longrightarrow \text{NHPh·NH·CMe:CH}_2 \longrightarrow$

$$\text{NH}_2\text{·C}_6\text{H}_4\text{·CH:CMe·NH}_2,\text{HCl} \longrightarrow \text{C}_6\text{H}_4{<}^{\text{CH}}_{\text{NH}}{>}\text{CMe} + \text{NH}_4\text{Cl},$$
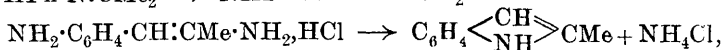
the authors record the process of reasoning which led them to expect that azines of substances containing the group ·CH$_2$·CO· would, under correct conditions, be transformed into pyrroles. Their expectation was fulfilled in the case of phenylbenzylketazine, which yielded tetraphenylpyrrole and ammonium chloride when heated at 180° in a current of dry hydrogen chloride. The simple aliphatic azines, such as acetaldazine and dimethylketazine, yield the corresponding pyrazoles and pyrazolines.

Ketazines are obtained in excellent yield by heating the ketone with the calculated quantity of hydrazine sulphate in boiling aqueous alcohol in the presence of an excess of sodium acetate.
                                                                    C. S.

Course of the Reaction between Diacetyl [Dimethyl Diketone] Monoxime and Aldehydes in the Presence of Ammonia. Formation of Dihydroxydihydroglyoxalines. OTTO DIELS (*Ber.*, 1918, 51, 965—976).—The author has already shown that when dimethyl diketone monoxime is condensed with aldehydes in the presence of a concentrated alkali hydroxide, oximes of unsaturated αβ-diketones are formed, thus: R·CHO + COMe·CMe:N·OH = H$_2$O + R·CH:CH·CAc:N·OH (A., 1913, i, 875), whereas compounds of the type $\text{RC}{<}^{\text{O·CMe}}_{\text{N·CMe}}{>}\text{O}$ are produced if

concentrated hydrochloric acid is the condensing agent (A., 1915, i, 690). It is now found that a reaction also takes place in the presence of aqueous-alcoholic ammonia, the products being characterised by the fact that they readily lose water on warming and combine with it again most easily. As ammonia takes part in the reaction, it is assumed that the aldehydes condense with the oxime in the form of their ammonia compounds, and the process is indicated in the following way:

$$NH_2 \cdot CHR \cdot OH + COMe \cdot CMe \colon N \cdot OH \longrightarrow$$

$$N \underset{\text{CHR·N·OH}}{\overset{\text{CMe--CMe·OH}}{\diagdown}} \underset{+H_2O}{\overset{-H_2O}{\longrightarrow}} N \underset{\text{CHR·N---}}{\overset{\text{CMe--CMe}}{\diagdown}} O.$$
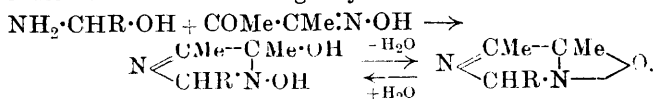
The products are therefore dihydroxydihydroglyoxalines.

For example, benzaldehyde yields the *compound*, $C_{11}H_{14}O_2N_2$, which crystallises in compact needles, forms colourless, crystalline salts with sodium hydroxide or nitric and sulphuric acids, and melts at 120—121° with evolution of water, thereby changing into the *compound*, $C_{11}H_{12}ON_2$, m. p. 180°. On oxidation with dilute chromic acid, it yields acetic and benzoic acids and 3-*phenyl*-5-*methyl*-1 : 2 : 4-*oxadiazole*, $O \underset{\text{CMe:N}}{\overset{\text{N===CPh}}{\diagdown}}$, which has m. p. 41°, b. p. 252—253°/763 mm., and the odour of methyl salicylate, and is the "benzenylazoximethenyl" described by Tiemann and Krüger (A., 1884, 1326). On reduction with zinc dust and 50% acetic acid, it forms a *base*, $C_{11}H_{14}N_2$, which has m. p. 242°, sublimes readily, and gives well-defined salts with the mineral acids.

Furfuraldehyde reacts at about 40—60° to give the *compound*, $C_9H_{12}O_3N_2$, which crystallises from hot water in prisms, forms a crystalline hydrochloride and sulphate, dissolves in dilute alkali hydroxides, gives a pale amethyst solution in concentrated sulphuric acid which is changed to emerald-green on adding a trace of nitric acid, melts at 112—113°, losing water and changing into the *compound*, $C_9H_{10}O_2N_2$, m. p. 170—171°. At 0°, the product is hydrofurfuramide, which does not react further with dimethyl diketone monoxime unless the mixture is warmed with a little free ammonia.

Cinnamaldehyde forms the *compound*, $C_{13}H_{16}O_2N_2$, which crystallises in glistening, pale yellow prisms, m. p. 138—139° (decomp.), and gives very sparingly soluble salts with the mineral acids.

Acetaldehyde-ammonia and dimethyl diketone monoxime yield the *compound*, $C_{10}H_{17}O_3N_3$, in large crystals, m. p. 129—130°. This seems to be loosely compounded of one molecule of the oxime and the expected *compound*, $C_6H_{12}O_2N_2$, analogous to the above (R = Me), which crystallises in druses, m. p. 80—81°, and loses water to form the *compound*, $C_6H_{10}ON_2$, m. p. 134°, for resolution into these two products can be effected by warming with water, alkalis, acids, or phenylhydrazine.   J. C. W.

Nature of Cyclic Quinoneimide Dyes. F. KEHRMANN (*Annalen*, 1917, **414**, 131—188).—A theoretical paper containing a discussion of the results of investigations of the constitutions of

cyclic quinoneimine dyes. The classes discussed are azonium compounds (azines, safranines, indulines), azthionium (thionines), azoxonium (azoxines), carboxonium and carbothionium (pyronines, rosamines, thiopyronines, cyanopyronines, cyanoacridines), and acridonium. The discussion starts with the desmotropy of 6-hydroxynaphthaphenazine recorded by Kehrmann and Messinger in 1891, and this strikes the key-note of the author's treatment of the subject. The dyes are in general regarded as desmotropic substances which acquire the ortho- or the para-quinonoid structure according to the conditions; for example, rosinduline and induline salts are orthoquinonoid, but the free bases are paraquinonoid.

C. S.

Constitution of Pyronine. J. VON BRAUN (*Ber.*, 1918, **51,** 440—441).—Polemical, replying to Kehrmann's references (preceding abstract) to the author's views (A., 1916, i, 663).

J. C. W.

Acylated *p*-Phenylenemethyldiamines. GILBERT T. MORGAN and WILLIAM ROBINSON GRIST (T., 1918, **113**, 688—694).—Acyl derivatives of *p*-phenylenediamine are of technical importance for the production of bisazo-dyes. The following intermediates have been prepared from methylaniline: p-*nitromethylformanilide,* $NO_2 \cdot C_6H_4 \cdot NMe \cdot CHO$, pale yellow prisms, m. p. 118—120°; p-*aminomethylformanilide* (as-*formyl*-p-*phenylenemethyldiamine*), colourless needles, m. p. 132°; the corresponding *acetanilide,* colourless needles, m. p. 63°. The last two substances by treatment with nitrous anhydride in dry acetone at $-10°$ yield *formylmethylaminobenzene-4-diazohydroxide,* $CHO \cdot NMe \cdot C_6H_4 \cdot N_2 \cdot OH$, greyish-white granules, decomp. 131—132°, and the corresponding *acetyl* compound, decomp. 131—132°, respectively, which react with dry β-naphthol to form *formylmethylaminobenzene-4-azo-β-naphthol,* ill-defined crystals, m. p. 160—161°, and the corresponding *acetyl* compound, red tablets or flattened needles, m. p. 139°; the two azo-β-naphthols were also obtained by coupling the diazotised *p*-aminomethylacylanilides with β-naphthol in alkaline solution.

C. S.

Preparation of 4-Diallylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (D.R.-P., 304983; from *Chem. Zentr.,* 1918, i, 789).—4-Diallylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone, colourless crystals, m. p. 90°, possessing antipyretic and narcotic effect, is obtainable by the action of allyl haloids on 4-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone in the warm, preferably in the presence of a solvent or diluent, and with the addition of some substance to remove the acid produced.

D. F. T.

Theory of Ring Closure. RICHARD MEYER and HERMANN LÜDERS (*Annalen,* 1918, **415**, 29—50).—Since Thiele and Falk (A., 1906, i, 750) have shown that Anderlini's so-called *o*-phenylene-

phthalamide, prepared from *o*-phenylenediamine and phthalic acid
(A., 1894, i, 3í5), is really 2-carboxyphenylbenziminazole, the
authors have reinvestigated the action of *o*-phenylenediamine with
succinic acid, and find that two compounds only are formed, not
three as stated previously (A., 1903, i, 442; 1906, i, 765), the sub-
stance, m. p. 236°, supposed to be the 8-ring *o*-phenylenesuccin-
amide being identical with benziminazole-2-propionic acid. It
yields a *methyl* ester, quadratic leaflets, m. p. 144—145°, *ethyl*
ester, needles, m. p. 135—136°, and *amide*, prismatic needles, m. p.
254° (decomp.); the *silver* salt, small prisms, *copper* salt, blue
plates, and *platinichloride*, yellow crystals, are described, and also
the *platinichloride* of the methyl ester. By heating at 230—240°,
it loses water and yields 1 : 2-*propionylenebenziminazole*,

$$\begin{array}{c} N\text{===}C\cdot CH_2 \\ \overset{|}{C_6H_4\cdot}\overset{|}{N}\text{---}CO \end{array}\!\!>\!\!CH_2,$$
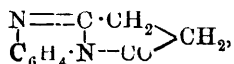
colourless needles, m. p. 171°.

Since, therefore, the compounds obtained from *o*-phenylene-
diamine and phthalic acid and succinic acid respectively are 5-ring,
not 8-ring compounds, the behaviour of the diamine with other
dibasic acids (Meyer, *loc. cit.*) requires reinvestigation. Cox (*Diss.,*
Strassburg, 1908) has already shown that the product from the
diamine and malonic acid is easily split into its generators, does not
contain a carboxyl group, and is the 7-ring *o*-phenylenemalonamide,
as stated by Meyer. It is now shown that the product from
o-phenylenediamine and ethyl *iso*succinate behaves similarly, and
is, as stated previously (*loc. cit.*), the 7-ring *o*-phenylene*iso*-
succinamide, although its infusibility and sparing solubility suggest
that the molecule is polymerised.

The reactivity of the methine hydrogen atom in ethyl *iso*succinate
has been investigated. No reaction occurs with formaldehyde or
benzaldehyde, and the sodio-derivative of the ester does not yield
condensation products with succinyl chloride or phthalyl chloride,
but reacts with benzoyl chloride and with cinnamoyl chloride in
dry ether to form *ethyl α-benzoyliso*succinate, $CMeBz(CO_2Et)_2$,
small, quadratic plates, m. p. 36—38°, b. p. 193—195°/18 mm.,
and *ethyl α-cinnamoyliso*succinate, a pale yellow, viscous liquid,
b. p. 225—230°/15 mm., respectively. *iso*Succinic acid and benzoic
or cinnamic acid are obtained when attempts are made to hydrolyse
these esters, and the reaction with phenylhydrazine results in the
formation of benzoyl- or cinnamoyl-phenylhydrazine and ethyl
*iso*succinate.

When heated slowly, *m*-nitrophthalanilic acid apparently has
m. p. 240° (Meyer, *loc. cit.*), but when heated rapidly it melts at
202° with violent foaming (Tingle and Rolker, A., 1909, i, 28),
resolidifies, and melts again at 240°. This phenomenon is due to
the conversion of the anilic acid into the anil, which has m. p.
240—242°. The anilic acid crystallises in colourless needles, not
faintly yellow, as previously stated (Meyer, *loc. cit.*). The fusion
of *p*-nitrophthalanilic acid is similar; at 190—192° fusion occurs

with violent foaming, and the product resolidifies and melts again
at 260°, the m. p. of the anil. o-Nitrophthalanilic acid, yellow
leaflets, has m. p. 146—148° (without decomp.), but at 190—200°
it loses water and yields the anil, colourless needles, m. p.
200—201°. m-Nitrosuccinanilic acid has m. p. 179° (stated
previously, 181—182°, *loc. cit.*), and the anil has m. p. 174°.

C. S.

**Action of Ortho- and of Peri-diamines, and of Ethylene-
diamine, on γ-Lactones.** A. BISTRZYCKI and WALTHER SCHMUTZ
(*Annalen*, 1918, **415**, 1—28).—The behaviour of o-phenylene-
diamine and of 1 : 8-naphthylenediamine with lactones derived from
certain alcohol-acids has been examined; two molecules of water
are eliminated and benziminazole derivatives produced. When
lactones derived from phenolic acids are employed, benziminazole
derivatives are again obtained, but the condensation does not
proceed beyond the elimination of one molecule of water. Thus
phthalide and o-phenylenediamine hydrochloride, heated at from
about 180° to 200°, yield the hydrochloride of o-benzylenebenz-
iminazole, m. p. 212—213° (Thiele and Falk, A., 1906, i, 751, give
210°) ·(*picrate*, yellow needles, decomp. 243·5°), whilst phthalide
and 1 : 8-naphthylenediamine in a similar reaction yield the hydro-
chloride of benzyleneperimidine (phthaloperine). Whilst phthalo-
phenone does not react with o-phenylenediamine (or its hydro-
chloride) or with p-ethoxy-o-phenylenediamine, phenolphthalein
reacts extremely vigorously with the former at 230°, yielding
di-p-hydroxyphenylbenzylenebenziminazole,

$$\begin{array}{l} C(C_6H_4 \cdot OH)_2 \cdot N \cdot C_6H_4 \\ C_6H_4 \underline{\qquad} C:N \end{array}$$

needles, decomp. 354—355°, which gives a colourless solution in
dilute aqueous potassium hydroxide, and forms a *picrate*, stout
prisms, m. p. 203—204°, and *diacetate*, best isolated in the form of
the *picrate*, $C_{36}H_{25}O_{11}N_5$, yellow needles, decomp. 285·5—286°.
When a mixture of valerolactone and o-phenylenediamine is heated,
finally at 270°, 1 : 2-(1′-*methyltrimethylene*)-*benziminazole,*

$$CH_2 < \begin{array}{l} CHMe \cdot N \cdot C_6H_4 \\ CH_2 \underline{\quad} C:N \end{array}.$$
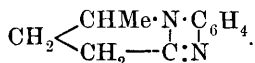
is obtained in bad yield as a brown oil; the *picrate*, yellow, micro-
scopic prisms, has m. p. 222—224° (darkening).

o-Phenylenediamine and the lactone of o-hydroxydiphenylacetic
acid react quantitatively at 120—130° to give 2-o-*hydroxybenz-
hydrylbenziminazole,* $C_6H_4 < \begin{array}{l} N \\ NH \end{array} > C \cdot CHPh \cdot C_6H_4 \cdot OH$, m. p.
246—247°, which separates from ethyl alcohol or benzene in micro-
scopic, colourless leaflets containing 1 mol. of solvent, and forms
a *picrate*, stout, yellow prisms, m. p. 216°, with previous darken-
ing; attempts to eliminate a second molecule of water by fusion
with phosphoric oxide or zinc chloride were unsuccessful. The
same lactone reacts with p-ethoxy-o-phenylenediamine to form

4(or 3)-*ethoxy-2-o-hydroxybenzhydrylbenziminazole*,

$$C_{22}H_{20}O_2N_2,H_2O,$$
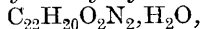
colourless prisms, m. p. 110—120°, with loss of the water of crystallisation, with 1 : 8-naphthylenediamine at 70—100° to form

2-*o-hydroxybenzhydrylperimidine*, $C_{10}H_6\diagdown\!\!\!\!\!\!\!\!\underset{NH}{\overset{-N}{\diagup}}\!\!\!\!\!\!\!\!\diagup C\cdot CHPh\cdot C_6H_4\cdot OH$,

colourless, microscopic plates, m. p. 295—297° (decomp.), and with 1 : 2-naphthylenediamine at 120—140° quantitatively to form 2-*o-hydroxybenzhydrylnaphthiminazole*, $C_{24}H_{18}ON_2$, colourless, microscopic prisms, m. p. 294—295°, in which it has not been determined whether the NH-group is attached to the naphthalene nucleus in the α- or the β-position. The lactone of 2-hydroxy-5-methyltriphenyiacetic acid does not react with phenylenediamine or its hydrochloride.

The behaviour of ethylenediamine with lactones is quite different from that of aromatic diamines. When phthalide (2 mols.) dissolved in absolute alcohol is boiled with a 50% aqueous solution of ethylenediamine (1 or 2 mols.), an additive compound, NN′-*ethylenebis-(2-hydroxymethylbenzamide)*,

$$C_2H_4(NH\cdot CO\cdot C_6H_4\cdot CH_2\cdot OH)_2,$$
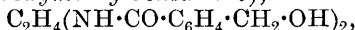
colourless needles, m. p. 183·5°, is obtained on cooling after pouring into water, which forms a *diphenylurethane*, $C_{32}H_{30}O_6N_4$, colourless needles, decomp. 190° (rapidly heated), when heated with phenylcarbimide at 160°, and is oxidised by chromic and glacial acetic acids to the dicarboxylic acid, which immediately changes to diphthalylethylenedi-imide by loss of water. The additive compound loses water above its m. p. and undergoes a partial change into NN′-*ethylenediphthalimidine*,

$$C_2H_4\Big(N\diagdown\!\!\!\!\underset{CO}{\overset{CH_2}{\diagup}}\!\!\!\!\diagup C_6H_4\Big)_2,$$
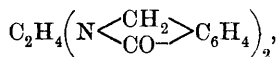
colourless prisms or needles, m. p. 227·5—229°, which is also obtained in 80—90% yield by heating phthalide (2 mols.) and ethylenediamine (1 mol.) at 300° for three hours. Ethylenediphthalimidine is quite stable to boiling aqueous or alcoholic potassium hydroxide. By treatment with boiling chromic and pure acetic acids, it can be oxidised successively to NN′-*ethylenephthalimidephthalimidine*,

$$C_6H_4\diagdown\!\!\!\!\underset{CO}{\overset{CH_2}{\diagup}}\!\!\!\!\diagup N\cdot CH_2\cdot CH_2\cdot N\diagdown\!\!\!\!\underset{CO}{\overset{CO}{\diagup}}\!\!\!\!\diagup C_6H_4,$$
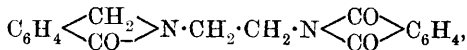
colourless needles, m. p. 190—191°, and to *NN′*-ethylenediphthalimide (diphthalylethylenedi-imide, Anderlini, A., 1894, i, 490). The former of these is hydrolysed by hot, moderately dilute aqueous potassium hydroxide to NN′-*ethylenephthalimidine-o-carboxybenz-amide*, $C_6H_4\diagdown\!\!\!\!\underset{CO}{\overset{CH_2}{\diagup}}\!\!\!\!\diagup N\cdot CH_2\cdot CH_2\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, colourless prisms, decomp. 172—173° (*silver* salt, $C_{18}H_{15}O_4N_2Ag$, tufts of needles).

When treated with bromine (2 mols.) in glacial acetic acid solu-

tion, which is then boiled for a few minutes, ethylenediphthal-
imidine yields a *tribromide*, $C_{18}H_{16}O_2N_2Br_3$, unstable, yellowish-
brown needles, decomp. 187° (rapidly heated), which is immedi-
ately decomposed by water with regeneration of the diphthal-
imidine. Chlorine does not attack ethylenediphthalimidine in
glacial acetic acid or carbon tetrachloride, but in the former solvent
together with ethyl ether iodine produces a *di-iodide*, $C_{18}H_{16}O_2N_2I_2$,
dark brown prisms, m. p. 180—181°.

Ethylenediphthalimidine is converted into diphthalylethylenedi-
imide by boiling with phosphorus pentachloride and phosphoryl
chloride, and by heating with sulphur at 240—250° until hydrogen
sulphide ceases to be evolved, yields 1:2:4:3-*dibenzoylene*-
1:4:5:6-*tetrahydropyrazine* (annexed formula), brownish-orange
needles, m. p. 202—203°. This substance, which
is more easily obtained by heating a mixture of
phthalide, ethylenediamine, and sulphur in a sealed
tube at 250°, is oxidised to diphthalylethylenedi-
imide by chromic and acetic acids.
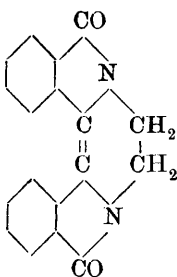
Ethylenediamine (anhydrous or in 50% aqueous
solution) reacts vigorously with the lactone of
o-hydroxyphenylacetic acid (2 mols.), and it is pre-
ferable to add alcohol as a diluent; the product is
NN'-*ethylenebis-(o-hydroxyphenylacetamide)*,

$$C_2H_4(NH \cdot CO \cdot CH_2 \cdot C_6H_4 \cdot OH)_2,$$
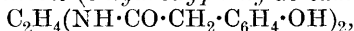
colourless needles, m. p. 208°, which forms a
diphenylurethane, $C_{32}H_{30}O_6N_4$, needles, m. p. 225°. Still more
vigorously react 50% aqueous ethylenediamine and the lactone of
o-hydroxydiphenylacetic acid, and alcohol must be added to keep
the reaction under control; the product is N-o-*hydroxydiphenyl-
acetylethylenediamine*, $OH \cdot C_6H_4 \cdot CHPh \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot NH_2$,
colourless needles, decomp. 197°, whether 1 or 2 mols. of the lactone
is present.   C. S.

Histidine and Carnosine.   The Synthesis of Carnosine.
LOUIS BAUMANN and THORSTEN INGVALDSEN (*J. Biol. Chem.*, 1918,
35, 263—276).—The amino-radicle may be removed from carnosine
by treatment in aqueous solution with barium nitrite and sulphuric
acid. After hydrolysis, by boiling with sulphuric acid, 70% of
the theoretical quantity of histidine can be isolated from the
deaminised product. Carnosine must therefore be regarded as
β-alanylhistidine,

$$\genfrac{}{}{0pt}{}{NH \cdot CH}{CH=N}{>}C \cdot CH_2 \cdot CH(NH \cdot CO \cdot CH_2 \cdot CH_2 \cdot NH_2) \cdot CO_2H,$$

instead of the other possible isomeride, histidyl-β-alanine,

$$\genfrac{}{}{0pt}{}{NH \cdot CH}{CH=N}{>}C \cdot CH_2 \cdot CH(NH_2) \cdot CO \cdot NH \cdot CH_2 \cdot CH_2 \cdot CO_2H.$$
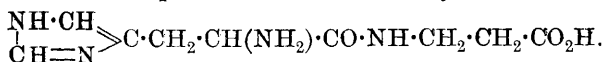
This conclusion has been confirmed by the synthesis of carnosine.
A solution of β-iodopropionyl chloride in light petroleum is added

slowly to histidine dissolved in water, an alkaline reaction being maintained throughout by the addition of barium hydroxide. The reaction product is not isolated, but after the removal of the barium by means of carbon dioxide, the filtrate is saturated with ammonia, first in the cold and eventually in sealed tubes at 100°. By fractional precipitation with silver nitrate and barium hydroxide, about 3 grams of pure carnosine were obtained from 40 grams of histidine.

By a similar method, β-iodopropionylalanine,

$$CH_2I \cdot CH_2 \cdot CO \cdot NH \cdot CHMe \cdot CO_2H,$$
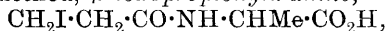
is prepared by the interaction of α-alanine and β-iodopropionyl chloride. It melts at 153—155°.

Extracts of dog's liver and muscle, which readily hydrolyse certain dipeptides, do not hydrolyse carnosine.

Attempts to prepare histidyl-β-alanine, or derivatives of it, have not been successful. By the action of α-naphthalenesulphonyl chloride on histidine in alkaline solution, α-naphthalenesulphonyl-histidine naphthalenesulphonate, $C_{26}H_{23}O_7N_3S_2, H_2O$, is obtained, which melts at 155°, and, on further heating, solidifies, and melts again at 220°. By heating at 150° over phosphoric oxide in a vacuum, the molecule of water is removed, and the anhydrous substance crystallises in long, prismatic rods from methyl alcohol containing a few drops of glacial acetic acid, and melts at 222°. By treatment of its alcoholic solution with sodium hydroxide, the compound yields α-naphthalenesulphonylhistidine,

$$C_{16}H_{15}O_4N_3S, H_2O,$$

m. p. 236°, $[\alpha]_D^{24} - 190 \cdot 8°$.

Hippuryl-β-alanine, $C_{12}H_{14}O_4N_2$, is readily prepared by the interaction of β-alanine and hippuryl chloride in alkaline solution. It crystallises in long needles, m. p. 183—185°. H. W. B.

Crystalline Form of 3 : 7-Dimethyl-1 : 9-diethyluric Acid and of its Glycol Dimethyl Ether. A Correction. HEINRICH BILTZ and FRITZ MAX (*Annalen*, 1917, **414**, 255).—The description of the crystalline form of 3 : 7-dimethyl-1 : 9-diethyluric acid (A., 1917, i, 590) is really that of its glycol dimethyl ether. The former crystallises in small rhombohedra with blunted angles.

C. S.

Azo-dyes derived from *m*-Phenetidine. FRÉD. REVERDIN, AUG. RILLIET, and CAM. VERNET (*Arch. Sci. phys. nat.*, 1918, [iv], **46**, 74—80).—Benzenediazonium chloride combines with *m*-phenetidine to give 4-*benzeneazo-m-phenetidine*
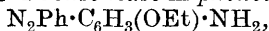
$$N_2Ph \cdot C_6H_3(OEt) \cdot NH_2,$$

m. p. 84—85°, yielding a *hydrochloride*, m. p. 152—153°, an *acetyl* derivative, m. p. 135°, and a *benzoyl* derivative, m. p. 146°. This base, when further diazotised and combined with β-naphthol, gives the *bisazo*-compound, $N_2Ph \cdot C_6H_3(OEt) \cdot N_2 \cdot C_{10}H_6 \cdot OH$, brown needles, m. p. 172°, with " R-salt," the *bisazo*-compound,

$$N_2Ph \cdot C_6H_3(OEt) \cdot N_2 \cdot C_{10}H_4(SO_3H)_2 \cdot OH,$$
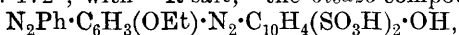
a reddish-violet powder, dyeing silk and wool reddish-violet, and with naphthionic acid the *bisazo*-compound,

$$N_2Ph \cdot C_6H_3(OEt) \cdot N_2 \cdot C_{10}H_5(SO_3H) \cdot NH_2,$$
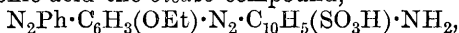
a blackish-brown powder, dyeing silk a reddish-brown, not fast to light. The base has also been diazotised and combined with 7-amino-1-naphthol-3-sulphonic acid, 1:8-dihydroxynaphthalene-3:6-disulphonic acid, 3-amino-2-naphthol-6-sulphonic acid, 2-naphthol-7-sulphonic acid, 1-naphthol-4-sulphonic acid, and 8-amino-1-naphthol-3:6-disulphonic acid.

Aniline-*m*-sulphonic acid similarly furnishes m-*sulphobenzene-azo*-m-*phenetidine*, $SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OEt) \cdot NH_2$, reddish-brown needles, m. p. 214—215°. This base, when further diazotised, combines with *p*-nitrobenzeneazo - 8 - amino-1-naphthol-3 : 6-disulphonic acid to give the *trisazo*-compound,

$$SO_3H \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OEt) \cdot N_2 \cdot C_{10}H_2(OH)(NH_2)(SO_3H)_2 \cdot N_2 \cdot C_6H_4 \cdot NO_2,$$

as a blackish-green powder.

In the same manner, *p*-nitroaniline yields p-*nitrobenzeneazo*-m-*phenetidine*, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OEt) \cdot NH_2$, which, when diazotised and combined with chromotropic acid, gives the *bisazo*-compound, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OEt) \cdot N_2 \cdot C_{10}H_3(OH)_2(SO_3H)_2$, a blackish-brown powder, in which the nitro-group may be reduced by sodium sulphide, giving a brown powder, which dyes wool blue. *m*-Phenetidine does not apparently combine readily with diazonium salts of high molecular weight.   W. G.

Influence of Substituents on Reactions. I. The Rate of Reduction of Substituted Phenylhydrazines. HARTWIG FRANZEN (*J. pr. Chem.*, 1918, [ii], **97**, 61—92).—It is already known that derivatives of the aminophenylhydrazines and the ethoxyphenylhydrazines readily undergo fission at the –N–N–linking, the effect being less marked when the substituent group is in the meta-position than when in the ortho- or para-position (Franzen, A., 1907, i, 321; Franzen and Fürst, 1914, i, 206; 1917, i, 58, 59; Franzen and Schmidt, this vol., i, 81). The reduction of substituted phenylhydrazines by stannous chloride and hydrochloric acid appears to be parallel to the above fission reaction in its susceptibility to influence by substituents, but, being more rapid, is more convenient for experimental investigation in the less reactive compounds. Examination of the rate of reduction of phenylhydrazine and its various methyl, chloro-, bromo-, iodo-, carboxylic, and sulpho-derivatives shows that the first four radicles which direct further substituents into the ortho- and para-positions, when in the 2- or 4-position to the hydrazine nucleus, increase the rate of reduction of phenylhydrazine, whereas the last two radicles, which direct further substituents into the meta-position, effect a diminution in the rate of reduction, whether they are in the 3- or 4-position. Radicles of the former class, with the exception of methyl, when in the 3-position likewise increase the velocity of reduction, but the effect is always less than that of the same radicle in the ortho- or para-position, thus corresponding with the observa-

tions already made on the ethoxy- and amino-phenylhydrazines.
With the second group of substituents, the influence is always
greater in the meta- than in the para-position; the ortho-compounds
in these cases were not investigated, because their tendency to ring
formation gives rise to complications. With methyl, chlorine, and
bromine the influence is greater in the ortho- than in the para-
position, but with iodine and ethoxyl the case is reversed. When
placed in order of the magnitude of their influence, the relative
position of the substituents is $NH_2 > OEt > Me,I > Br,Cl$, the
substituents methyl and iodine, as also bromine and chlorine,
possessing almost equal influence. A striking parallel exists
between the tendency of these substituents to facilitate further
substitution at the ortho- and para-positions, in which positions of
the phenylhydrazine molecule they themselves increase the reactivity
of the substance, whilst the class of substituents including the
carboxylic and sulpho-groups reduces the tendency of a compound
to further substitution, and directs the new group into the meta-
position, in which position of the phenylhydrazine molecule they
cause the least diminution in the reaction velocity. It is also of
interest that the relative effect of the substituents amino, hydroxyl,
methyl, chlorine, on the reduction of the aromatic halogen com-
pounds by hydriodic acid falls into a similar order to that above
(Klages and Liecke, A., 1900, i, 387). In view of the preceding
results, Vorländer's conclusion (A., 1903, ii, 67), that the unsatu-
rated groups in particular possess the power of increasing the re-
activity of the substituted compound, is unjustified; this criticism
is confirmed by the peculiarity that the nitro-group in 1-chloro-2 : 4-
dinitrobenzene increases the reactivity of chlorobenzene towards
ammonia, but not towards hydrogen, whereas the presence of the
amino- or hydroxyl group barely affects the former reaction, but
favours the latter. The author is of opinion that the increase in
the reactivity of phenylhydrazine induced by any such radicle as
the amino-group or hydroxyl group is due to the unsaturated
nature of the main atom by which it is attached to the benzene
ring, and further evidence in support of this view is adduced from
the behaviour of 4-hydrazinostilbene, the investigation of which
places the $CHPh:CH$-radicle between OEt and Me in the above
order of influence; the phenyl radicle falls into the same position
as the styryl radicle, as is indicated by an investigation of 4-hydr-
azinodiphenyl. The conclusion is therefore drawn that the series
$NH_2 > OEt > Ph.CHPh:CH > Me.I > Br,Cl$ represents also the
relative degree of unsaturation of the radicles concerned, and that
the groups $\cdot SO_3H$ and $\cdot CO_2H$, which effect a reduction in the
reactivity of phenylhydrazine, are in an especially saturated con-
dition. On investigation of the reaction of benzyl chloride and its
three methyl derivatives with sodium ethoxide, it is found that the
case resembles that of phenylhydrazine and the tolylhydrazines,
the ortho-derivative being more reactive than the para-compound,
and both of these more reactive than the meta-derivative, which
indeed is but little more reactive than the parent compound.

Evidence of a similar but less simple nature is supplied by the behaviour of phenyl acetate and the three tolyl acetates towards alcoholic sodium ethoxide, although on account of the presence of water in the commercial alcohol used, the change observed was one of hydrolysis; the relative reactivity of the parent phenyl compound and its three methyl derivatives is identical with that of benzyl chloride and its methyl derivatives.

4-*Hydrazinostilbene*, CHPh:CH·C$_6$H$_4$·NH·NH$_2$, was obtained in the form of its *hydrochloride*, pearly leaflets, m. p. 254° (decomp.), from 4-aminostilbene by successive diazotisation and reduction; *benzylidene* derivative, C$_{21}$H$_{18}$N$_2$, yellow, crystalline powder, m. p. 208° (decomp.); *dibenzoyl* derivative, C$_{28}$H$_{22}$O$_2$N$_2$, colourless leaflets, m. p. 195°. When heated with dilute hydrochloric acid, the base yields 4-aminostilbene, stilbene, ammonia, and nitrogen. 4-Hydrazinodiphenyl under similar conditions yields only 4-aminodiphenyl and ammonia.   D. F. T.

Aminohydrazines. V. *m*-Amino-*p*-tolyl-β-benzylhydrazine.

HARTWIG FRANZEN and COELESTIN MONDLANGE (*Annalen*, 1917, **414**, 189—195. Compare A., 1917, i, 58, 59).—This aminohydrazine has been examined in order to ascertain whether the yellow colour and the capacity to form intensely coloured salts exhibited by *o*-aminophenyl-β-benzylhydrazine (*loc. cit.*) are general characteristics of such aminophenylbenzylhydrazines.

Benzaldehyde-*m*-nitro-*p*-tolylhydrazone in boiling ammoniacal alcoholic solution is treated with sodium hyposulphite, whereby *sodium* m-amino-p-tolyl-β-*benzylhydrazinesulphonate* and *benzaldehyde-*m-amino-p-tolylhydrazone* are obtained, which are separated by boiling water, in which the former, pale yellow leaflets, m. p. 211° is insoluble. It is decomposed by boiling $N/2$-sulphuric acid, yielding sulphur dioxide and benzaldehyde-*m*-amino-*p*-tolyl-hydrazone, which is then converted into phenylmethylbenziminazole and ammonia. *Benzaldehyde-*m-amino-p-*tolylhydrazone*, obtained from the hot aqueous filtrate (above), forms golden-yellow leaflets, m. p. 167°, is converted by cold 10% hydrochloric acid into phenylmethylbenziminazole and ammonia, and in boiling alcoholic solution is reduced by 3% sodium amalgam, yielding m-*amino*-p-*tolyl*-β-*benzylhydrazine*, NH$_2$·C$_6$H$_3$Me·NH·NH·CH$_2$Ph, intensely yellow needles, m. p. 87°, which forms yellow solutions in organic solvents and develops in alcoholic solution an intense magenta colour on the addition of a little dilute mineral acid.   C. S.

Glacial Acetic Acid as a Solvent for Prussic Acid. Benzalhydrazinophenylacetonitrile and some Derivatives.

J. R. BAILEY and R. H. PRITCHETT (*J. Amer. Chem. Soc.*, 1918, **40**, 1230—1235).—Benzylidenehydrazinophenylacetonitrile,

CHPh:N·NH·CHPh·CN,
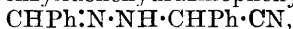
prepared by adding potassium cyanide to a solution of benzylideneazine in glacial acetic acid, forms colourless crystals, m. p. 114°

(Adamczewski, *Diss.*, Heidelberg, 1911, records yellow leaflets, m. p. 111—112°), and is converted by concentrated hydrochloric acid into the corresponding amide, m. p. 171° (to a yellow liquid) (Adamczewski, m. p. 165—167° with decomp.). The nitrile and the amide in glacial acetic acid solution are converted by potassium cyanate into *benzylidenecarbamylhydrazinophenylacetonitrile*, $CHPh\!:\!N\cdot N(CO\cdot NH_2)\cdot CHPh\cdot CN$, rectangular plates, m. p. 228° (decomp.), and the corresponding *amide*,

$$CHPh\!:\!N\cdot N(CO\cdot NH_2)\cdot CHPh\cdot CO\cdot NH_2,$$

prisms, m. p. 183° (decomp. at 193°), respectively. The latter is converted by boiling 10% potassium hydroxide and subsequent acidification with acetic acid into 1-*benzylideneamino-5-phenyl-hydantoin*, $NH{<}^{CO\cdot N\!:\!N\!:\!CHPh}_{CO\cdot CHPh}$, crystals, decomp. 245—250°, which loses benzaldehyde by heating with dilute sulphuric acid and yields 1-*amino-5-phenylhydantoin*, decomp. 232°.   C. S.

Pekelharing's Pepsin. IV. W. E. RINGER (*Arch. Néerland. Physiol.*, 1918, **2**, 571—593. Compare A., 1917, i, 233; 1916, i, 226).—In his previous experiments, the extent of proteolysis has been measured by the author by precipitating the proteins with tannic acid and estimating the nitrogen in the filtrate. It is now shown that these results are not quite accurate, because the amount of nitrogenous material precipitated by the tannic acid is found to vary considerably according to the concentration of the salts in the solution. The effect of the error is that the descent of the curve illustrating the course of the digestion is really less than has been represented. The former experiments have now been repeated, the concentration of salt being maintained constant. The optimum concentration of hydrogen ions for the digestion of the albumoses by pepsin varies from $p_H = 2\cdot5$ in the case of proto-albumose to 4·1 for deuteroalbumose. These results are in harmony with the view that a combination occurs between enzyme and substrate, because the smaller the hydrolytic product, the larger will be the number of particles in solution, and the sooner the moment will arrive (that is, the lower the degree of acidity) at which all the particles of enzyme are combined with particles of substrate, which according to the author constitutes the maximum point in the curve representing the hydrolysis.

The importance of the electrical charge of the protein in determining the course of proteolysis is illustrated by experiments in which the effect is ascertained of the addition of various potassium salts on the digestion of protein by pepsin. The strongly negative ferrocyanide ion inhibits proteolysis to a much greater extent than either the chloride or the sulphate.   H. W. B.

Action of Chymosin and Pepsin. IV. Action of the Enzymes on Sodium Caseinogenate. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 33—77. Compare A., 1915, i, 726, 911).—Two extracts of gastric mucous membrane may show

equal enzymic activity when tested by their power of coagulating milk, and yet show considerable differences in their digesting power on fibrin or white of egg. This want of parallelism is found also when the substrate chosen in each case is caseinogen, and the activity tested first in the presence of alkali and then in that of acid. In the former case, the solutions become opalescent and a precipitate forms, whilst albumoses are produced in considerable amount, and although there does not appear to be direct proportionality between the strength of the chymosin and the time in which the opalescence becomes of a definite degree or the precipitate is just perceptible, or between the quantity of chymosin present and the amount of albumose produced in a given time, yet the relative strengths of two chymosin solutions may be compared in either of these ways. The results can be interpreted most easily by regarding chymosin and pepsin as separate enzymes, and this view is confirmed by the fact that the differences observed between the coagulating and digesting powers of two extracts are exactly paralleled by the differences in their behaviour towards caseinogen in alkaline and acid solutions respectively. Thus, if one of two solutions of equal peptic power clots milk with greater rapidity than the other, then its action on caseinogen in alkaline solution is found to be much more marked and rapid than is the case with the other enzymic solution. H. W. B.

Digestibility of Heated and Unheated Caseinogen. OLOF HAMMARSTEN (*Arch. Néerland. Physiol.*, 1918, **2**, 658—663).— When caseinogen is dissolved in water with the addition of the minimum amount of alkali and the solution heated for an hour in an autoclave at about 116°, a small quantity of albumose is formed, whilst the recovered caseinogen is found to be more readily digested than unheated caseinogen by pepsin in the absence of free hydrochloric acid (negative reaction with Congo-red). The inability of heated milk to maintain the growth of young rats (Funk and Macallum, A., 1916, i, 861) cannot therefore be ascribed to an altered structure in the constituent amino-acids of the caseinogen caused by the heating, and resulting in failure of digestion and utilisation in the body. These results indirectly confirm the hypothesis of the existence of thermolabile indispensable accessory substances in milk. H. W. B.

Influence of Neutral Salts on the Action of the Salivary Diastase. J. TEMMINCK GROLL (*Arch. Néerland. Physiol.*, 1918, **2**, 516—520).—Both the anion and the cation of a neutral salt exert an action on ptyalin, the former being the more potent. The order in which the cations may be arranged expressing their relative activating power corresponds with that in which they affect colloids generally. The order of the anions, however, differs from that which would be expected if the diastase was a simple colloid. Neutral salts affect, therefore, not only the degree of dispersion of the ptyalin, but have another action, depending probably on the colloidal state of the substratum. H. W. B.

Enzymes and Surface Action. W. M. Bayliss (*Arch. Néerland. Physiol.*, 1918, **2**, 621—624).—The action of enzymes consists in the condensation on their surfaces by adsorption of the constituents of the reacting systems, including water. The effect of this concentration is to increase the rate at which the reactions take place and to diminish greatly the time taken for equilibrium to be attained. If the rate of action of an enzyme, such as urease, is a function of the amount adsorbed, the presence of an indifferent substance, which is adsorbed to a greater extent than carbamide, should delay the reaction. Saponin is adsorbed by charcoal to a greater extent than carbamide, and more carbamide is adsorbed by a given weight of charcoal from a pure carbamide solution than from one containing a mixture of carbamide and saponin. Applying these results to urease, it is found that the addition of saponin to a solution of carbamide containing urease delays the rate of action of the enzyme, although eventually the extent of hydrolysis of the carbamide is equal to that attained in the absence of the saponin. Bile salts and amyl alcohol produce similar effects. The inhibiting effect of saponin is greater at a low temperature than at a higher one, and the temperature coefficient of the reaction is increased, both phenomena being in harmony with the view that the saponin exerts its action by adsorption. The author's hypothesis does not seem to account for the specificity of enzymes, but without attempting to disregard this difficulty, he points out that the surface forces controlling adsorption are as yet too little known to warrant a dogmatic statement on this question.

<div align="right">H. W. B.</div>

Some Naphthalene Derivatives. A. Archibald Boon and James Ogilvie (*Pharm. J.*, 1918, **101**, 129—130).—When arsenic acid is heated with an arylamine, the latter may undergo oxidation, as in the preparation of magenta, or it may undergo conversion into an arylarsinic acid, $AsRO(OH)_2$, or even a diarylarsinic acid, AsR_2O_2H. When an intimate mixture of equal parts of α-naphthylamine and arsenic acid is crystallised from hot water, *α-naphthylamine hydrogen arsenate*, $C_{10}H_7 \cdot NH_2, H_3AsO_4$, is obtained in long, colourless needles, m. p. 170°, which become purple on exposure to the atmosphere or when heated above 165°; the apparent molecular weight in alcohol is 156. If this arsenate is heated with four-ninths its weight of α-naphthylamine at 200° for a short time, 1-aminonaphthyl-4-arsinic acid is produced, together with an amorphous, purple *substance*, $C_{13}H_{11}ON$; this gives a violet solution in organic solvents, and is doubtless an oxidation product of the naphthylamine. The formation of the arsenate and its further conversion into an arsinic acid confirm the general view that the reaction yielding aminonaphthylarsinic acid occurs by the stages

$$C_{10}H_7 \cdot NH_2 \longrightarrow C_{10}H_7 \cdot NH_2, H_3AsO_4 \longrightarrow C_{10}H_7 \cdot NH \cdot AsO(OH)_2 \longrightarrow$$
$$NH_2 \cdot C_{10}H_6 \cdot AsO(OH)_2.$$
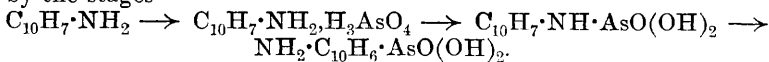
<div align="right">D. F. T.</div>

Physiological Chemistry.

Estimation of Buffer Effects in Measuring Respiration.
W. J. V. OSTERHOUT (*J. Biol. Chem.*, 1918, **35**, 237—240).—The
indicator method of measuring respiration (Haas, A., 1917, i, 433)
consists in placing organisms in a solution containing an indicator
and observing changes in colour produced by the giving off of
carbon dioxide. Since the acidity and colour are affected by sub-
stances having a buffer action, it is evident that when such sub-
stances are present the amount of buffer action must be measured.
This can be done by the apparatus described by the author, which
permits the addition of measured quantities of carbon dioxide to
known volumes of liquid of which the p_H values are estimated
before and after the addition of the carbon dioxide.   H. W. B.

**Estimations of the Tension of Carbon Dioxide in the
Alveolar Air by the Henderson-Russel Modification of
Haldane's Method, and their Application for Testing the
Stimulability of the Breathing Centre.** EUGEN JENNI
(*Biochem. Zeitsch.*, 1918, **87**, 331—358).—By means of the modifi-
cation by Henderson and Russel of Haldane's method, it was found
that the carbon dioxide tension of alveolar air remained constant
over prolonged periods. When the subject of experiment is used
to the procedure, the variations amount to but 2—3 mm. of mer-
cury; the method is not, however, well adapted to clinical purposes.
In a case of emphysema investigated, the tension of carbon dioxide
was high. The method can be employed for testing the irritability
of the breathing centre. For inhibition, the drugs morphine and
pantopone were employed; both cause marked increase in the tension
of carbon dioxide in the alveolar air. The preparation of Pavon-
Ciba, in corresponding therapeutic doses, causes little alteration in
the tension, and its inhibitory action on the breathing centre is
less than that of morphine or pantopone. Alcohol is an excitant of
the inhibitory centre in the doses used by the author.   S. B. S.

Narcosis and Oxygen Concentration. B. VON ISSEKUTZ
(*Biochem. Zeitsch.*, 1918, **88**, 219—231).—The action of narcotics
is independent of the oxygen concentration, and there is no marked
difference in their action on tadpoles in water rich and poor in
oxygen. During narcosis, the oxygen respiration of tadpoles
diminishes from 18—40%. Ethylurethane and alcohol in
narcotising doses cause the same amount of diminution. Potassium
cyanide diminishes oxygen respiration to the extent of 30—40%
without producing paralysis. Increased partial pressure of oxygen
can increase the oxygen respiration of the tadpoles without inhibit-
ing the action of narcotics; in fact, the oxygen consumption of the
animals under deep narcosis in water rich in oxygen is greater

than that of non-narcotised animals in water with the normal
amount of oxygen. 　　　　　　　　　　　　　　　　S. B. S.

**Estimation of the Methyl Groups attached to Nitrogen
in the Blood.** A. Kossel and S. Edlbacher (*Arch. Néerland.
Physiol.*, 1918, **2**, 625—628).—The application of Pregl's micro-
analytical method for the estimation of the methyl groups attached
to nitrogen (see Edlbacher, this vol., ii, 336) to blood gives results
which indicate that the ratio N/Me ranges in normal blood from
about 17 to 20, which corresponds with about 5 methyl groups
per 100 atoms of nitrogen present. In a few cases of pathological
blood, the ratio is rather higher, reaching to 26 in pernicious
anæmia. The coagulated protein of the blood does not contain any
methyl attached to nitrogen, whilst the amount in caseinogen is
about 0·4%. 　　　　　　　　　　　　　　　　　　H. W. B.

Properties and Composition of Oöcytase. Guy W. Clark
(*J. Biol. Chem.*, 1918, **35**, 253—262. Compare Robertson, A.,
1912, ii, 573).—Preparations of oöcytase, the fertilising and
cytolysing substance in mammalian blood sera, have been obtained
containing protein as an impurity. On hydrolysis, oöcytase yields
hypoxanthine and a pentose, but only a trace of phosphoric acid.
The active constituent is destroyed by heat at a temperature
between 73° and 80°, and by prolonged contact with alcohol.
Oöcytase is neither hæmolytic, bactericidal, nor identical with alexin.
The characteristic fertilising and cytolysing properties are probably
to be associated with the nucleosidic structure of the oöcytase.
　　　　　　　　　　　　　　　　　　　　　　　　H. W. B.

**Existence in the Animal Body of Substances capable of
Fixing Alkaloids.** W. Storm van Leeuwen (*Arch. Néerland.
Physiol.*, 1918, **2**, 650—657).—Pilocarpine dissolved in rabbit's
serum does not excite a strip of intestinal muscle (cat) to the same
extent as an aqueous solution of pilocarpine containing the same
proportion of the drug. The neutralising effect of the serum only
appears slowly, and reaches its maximum in about twenty-four
hours. Sera from other animals are not so effective, that from the
dog being quite inert. The neutralising action is due to fixation
and not to destruction of the pilocarpine, because by suitable means
all the alkaloid may be subsequently extracted from the serum
and found to retain its original stimulating power in aqueous solu-
tion. The neutralising substances are present also in the liver and
other organs of the body, and it is to their presence in differing
amounts that the varying susceptibility of different animals to
alkaloids is probably due. 　　　　　　　　　　　　H. W. B.

**Calcium and Magnesium Metabolism. V. Effect of
Acid and other Dietary Factors.** Maurice H. Givens (*J. Biol.
Chem.*, 1918, **35**, 241—251. Compare this vol., i, 321).—Experi-
ments on two dogs are described, the results of which indicate that
the ingestion of either hydrochloric acid or sodium chloride pro-

duces a small increase in the elimination of calcium in the urine, although it does not appreciably affect the calcium balance. The excretion of magnesium is not affected in either case.   H. W. B.

Autolysis of Animal Tissues.   KARL GUSTAV DERNBY (*J. Biol. Chem.*, 1918, **35**, 179—219).—Yeast cells and various animal tissues (liver, spleen, pancreas, gastric mucous membrane, and leucocytes of dogs and pigs) all contain two kinds of proteolytic enzymes: (*a*) pepsin-like enzymes which hydrolyse proteins to peptones, but not further, and for the action of which the optimum hydrogen ion concentration is about $p_H = 3.5$; (*b*) enzymes similar to trypsin or erepsin, which attack only peptones or peptides, and hydrolyse them to amino-acids. The optimum hydrogen-ion concentration for the latter enzymes is about $p_H = 7.8$. In some tissues, one type of enzyme is present to a much greater extent than the other.

Autolysis in the case of the pancreas and the liver proceeds furthest when the p_H is maintained between .5 and 6, and appears to be due to the action of the above proteolytic enzymes, the maximum action being obtained when the degree of acidity is such that both types of enzymes are able to work simultaneously. Pieces of tissue which have been treated with weak acids and then transferred to an alkaline solution undergo autolysis much more readily than similar pieces placed straightway into the alkaline solution. This is due to the ability of the ereptic enzyme to break down the peptones formed by the peptic enzyme in the acid solution, although it is unable to hydrolyse the native protein.   H. W. B.

Co-ferment of Fermentation in the Animal Body. II. OTTO MEYERHOF (*Zeitsch. physiol. Chem.*, 1918, **102**, 1—32. Compare this vol., i, 242).—The co-enzyme of zymase appears to exist in almost all the tissues of the frog and rabbit. It is present in relatively the largest amount in frog's muscle; it is absent from blood-serum. It is most readily extracted by boiling water. Cold water extracts contain the co-enzyme, but an inhibitory substance is also present which is destroyed by boiling. The inhibitory substance exerts its action on zymase and not on the co-enzyme, and appears to be of a protein nature. The chemical properties of the co-enzyme in muscle resemble those associated with the co-enzyme in yeast. It is dialysable, not destroyed by boiling, precipitated by alcohol, adsorbed by charcoal, etc. The course of fermentation, using the muscle co-enzyme, is analogous to that observed when the co-enzyme from yeast is employed.

The respiratory substance (*loc. cit.*) which accelerates the oxidation process in muscle appears to be identical with the co-enzyme of yeast and muscle. A similar co-enzyme is also present in germinating peas.   H. W. B.

The Constituents of Alcoholic Extracts of Organs which are Active in Wassermann's Reaction. FRITZ SILBERSTEIN (*Biochem. Zeitsch.*, 1918, **88**, 1—12).—Extracts of incompletely

autolysed organs are more active as "antigens" in the Wassermann reaction than are extracts of the fresh organ. If autolysis, however, proceeds too far, the extracts become inactive. Neither the fraction soluble in alcohol, but insoluble in ether (soaps), nor the fractions soluble in alcohol, ether, and acetone (fatty acids, fats, and cholesterol) of either fresh or autolysed livers give a reaction as marked as the whole extract. The fraction from fresh organs containing the lipoids gives as good results as the whole extract of the partly autolysed organ. The best reaction, however, is obtained by a mixture of the lipoid fraction with equivalent amounts of the fraction containing the soaps, fatty acids, and cholesterol. Treatment of the organ with trypsin or steapsin destroys its power of giving antigens; this function of the organs is not, however, altered by their treatment with pepsin–hydrochloric acid, ricin–lipase, or with dilute acid or alkali. S. B. S.

Biology of Silicic Acid and Aluminium Oxide in Birds' Feathers. MAX GONNERMANN (*Zeitsch. physiol. Chem.*, 1918, **102,** 78—84. Compare A., 1917, i, 494).—Feathers almost always contain silicic acid and aluminium oxide. The amounts vary considerably in different birds, and appear to depend largely on the content of these substances in the food. The largest quantity of silicic acid found was in the feathers of the dove, *Columba palumbus* (77% of the total ash), whilst the feathers of the jay, *Corvus glandarius,* contained the most alumina (2·46%). Apparently, the feathers constitute a storing place for both substances.

H. W. B.

Relation of the Quality of Proteins to Milk Production. IV. E. B. HART and G. C. HUMPHREY [with D. W. SMITH] (*J. Biol. Chem.*, 1918, **35,** 367—383. Compare A., 1917, i, 608).—Similar experiments to those already described have been carried out, the results of which indicate an approximate equality and efficiency of the proteins of gluten feed and oil meal as supplements to the proteins of corn meal and clover hay, an increased supplementing effect for distiller's grains, and an inferior efficiency for cottonseed meal, taken in relation to the quality and quantity of milk produced. H. W. B.

Effect of Heat on the Citric Acid Content of Milk. Isolation of Citric Acid from Milk. H. H. SOMMER and E. B. HART (*J. Biol. Chem.*, 1918, **35,** 313—318).—Citric acid can be obtained from cows' milk, after freeing the latter from fat and protein, in the form of calcium citrate; it is present to the extent of about 0·2% of the milk or 2% of the milk solids. Citric acid is not destroyed or transformed into an insoluble salt by heating the milk even in an autoclave at 15 lb. pressure for one hour. The loss in anti-scorbutic power observed on heating milk is therefore not due to the destruction of citric acid, but to the inactivation of the anti-scorbutic vitamine.

To estimate citric acid in milk, the caseinogen is precipitated by a dilute sulphuric acid solution of mercuric sulphate and the filtrate treated with dilute potassium permanganate solution. The citric acid is oxidised to acetonedicarboxylic acid, which is precipitated by the excess of mercury sulphate. The mercury in the precipitate is estimated by dissolving in hydrochloric acid and titrating with potassium cyanide and silver nitrate, using potassium iodide as indicator.   H. W. B.

Attempt to Filter the Enzymes of Milk. JEAN PICCARD and MARY RISING (*J. Amer. Chem. Soc.*, 1918, **40**, 1275—1281).— Attempts have been made to sterilise milk by filtration so that it would be free from germs and suspended impurities, while the enzymes would be unchanged. Failure resulted because a filter could not be found with pores large enough to allow the passage through them of the colloidal enzyme without at the same time allowing the passage of bacteria.

In the course of the work it was found that the Schardinger enzyme remains in the liquid portion of the milk after the casein and the fat have been removed by a small amount of acid. If the casein is precipitated by stronger acids, the enzyme is precipitated with it, and by still more acid it is destroyed.   C. S.

Action of Sugars on Bronchial Secretion. D. Lo MONACO (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 103—109).—The fact that the subcutaneous injection of sugars in small doses largely increases, and in larger doses diminishes and may even entirely prevent, lactation in women, cows, goats, etc., and that similar modifications of other animal excretions are also produced in this way, has led the author to examine the effect of subcutaneous injection of sucrose on a patient exhibiting copious bronchial secretion. The injection was rapidly followed by a diminution in the amount of the bronchial secretion, which sometimes ceased completely, reappearing again when the injections were suspended. This effect of the injection of sugar may be of great importance in removing one of the principal causes of the spread of phthisis, namely, the ingestion and respiration of dried tubercular sputum.   T. H. P.

Decomposition of Muconic and Adipic Acids in the Animal Body. YOSHITANE MORI (*J. Biol. Chem.*, 1918, **35**, 341—351).—Muconic and adipic acids injected subcutaneously into rabbits are excreted to a large extent unchanged in the urine.
                                                H. W. B.

Formation of the Unsaturated Acids in the Animal Organism. I. Behaviour of *p*-Methoxyphenylpropionic Acid in the Organism of the Rabbit. IWAO MATSUO (*J. Biol. Chem.*, 1918, **35**, 291—296).—After the subcutaneous injection of *p*-methoxyphenylpropionic acid, anisic and glycylanisic acids were isolated from the urine, instead of the expected cinnamic acid derivatives (compare Dakin, A., 1909, ii, 684).   H. W. B.

Formation of *p*-Hydroxyphenyllactic Acid in the Animal Organism and its Relation to Tyrosine Catabolism. YASHIRO KOTAKE [with ZENJI MATSUOKA] (*J. Biol. Chem.*, 1918, **35**, 319—331).—When *l*-tyrosine or *p*-hydroxyphenylpyruvic acid is administered to rabbits or men, *l*-hydroxyphenyllactic acid appears in the urine, accompanied occasionally by small amounts of the *dl*-acid. The administration of *dl*-hydroxyphenyllactic acid is followed by the elimination of only the *d*-acid, the lævorotatory component being evidently destroyed to a certain extent in its passage through the body.   H. W. B.

Relation between Nutrition and the Formation of Kynurenic Acid from Tryptophan. ZENJI MATSUOKA (*J. Biol. Chem.*, 1918, **35**, 333—339).—The rate of formation of kynurenic acid from tryptophan is almost constant in the rabbit, the injection of 1 gram of tryptophan being followed by the elimination of between 0·2 and 0·3 gram of kynurenic acid in the urine. Apparently kynurenic acid is very stable in the animal body, and it cannot take the place of tryptophan for the maintenance of nutrition. The formation of kynurenic acid from tryptophan is not therefore profitable from the point of view of nutrition.
H. W. B.

The Biological Action of Convolvulin and Jalapin. G. HEINRICH (*Biochem. Zeitsch.*, 1918, **88**, 13—34).—These substances are like the saponins and agaricin in that they exert a hæmolytic action when they are in neutral solution. They are very sensitive to alkalis, however, and rapidly lose the hæmolytic action in the presence of a slight excess of alkali. The hæmolytic action could only be demonstrated in vitro, but not in vivo, as no blood appeared in the urine after intravenous or subcutaneous injection; neither was any purgative action observed. They are both specific poisons for fish. For purgative action, direct contact of the glucosides with the mucous membrane of the intestines is necessary. This action is also lost when the substances are treated with alkali, and the hæmolytic action can therefore be used in testing the value of preparations as drugs. They are less sensitive to the action of mineral acids, as, in spite of the hydrolysis which ensues, the purgative action is not lost. In this respect, they are similar to the saponins. Like the saponins, too, they are only incompletely resorbed in the alimentary tract, and appear unchanged in the fæces.   S. B. S.

The Influence of Temperature on the Capillary Activity of Narcotics. B. VON ISSEKUTZ (*Biochem. Zeitsch.*, 1918, **88**, 213—218).—Temperature alters the narcotic activity of indifferent narcotics in the same direction as it alters their capillary activity. Increase and decrease of the narcotic activity of the six substances investigated by H. H. Meyer can be ascribed not only to the difference produced in their distribution between water and organic

solvents on warming, but also to increase or decrease of their capillary activity. In the case of other poisons, increase of temperature can cause diminution of capillary activity, whilst their potency is enhanced.   S. B. S.

Combined Action of Narcotics and Potassium Cyanide on Water-fleas. F. J. J. BUYTENDYK (*Arch. Néerland. Physiol.*, 1918, **2**, 521—529).—Warburg's theory of the action of narcotics on living cells is based on the assumption that the narcotic produces a modification in the degree of dispersion of the colloids in the cell. The combined action of two narcotics might be expected to be equal to the sum of the actions of each separately. This is found to be the case when narcotics such as alcohol and chloroform are employed, but not when one of the narcotics is potassiur cyanide. Water-fleas live in 3% alcohol or 1·5% urethane for more than twenty-four hours; in a liquid containing 3% of alcohol and 1·5% of urethane, they do not live more than ten minutes. When alcohol and potassium cyanide are similarly tested, it is found that instead of alcohol increasing the toxicity of the cyanide, it actually diminishes it, and the smaller the percentage of alcohol in the mixture, between the limits 3% and $\frac{1}{8}$%, the greater is the neutralising effect on the cyanide. It is conceivable that the narcotic might repel the hydrocyanic acid from the surface of the cell, but the author does not consider that an explanation on these lines is adequate to explain the observed facts. Moreover, the author has been unable to detect any similar neutralising action of narcotics on the inhibition by potassium cyanide of the phototropic phenomena observable with the *Daphniidæ*.   H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Anaerobic Culture Volumeter. ZAE NORTHRUP (*J. Ind. Eng. Chem.*, 1918, **10**, 624—625).—A glass bottle is closed by a cork through which passes a glass tube extending nearly to the bottom of the bottle and having a small Berkefeld filter fixed to its lower end. The tube has a tap just above the cork, and the upper end of the tube passes through a cork which fits into the neck of an inverted tapped separating funnel. The bottle is provided with a small exit tube plugged with cotton wool. The separating funnel is filled with liquid culture medium, and a quantity of the latter is introduced into the bottle so as to cover the filter. After the filled apparatus has been sterilised, the culture containing gas-forming organisms is pipetted into the stem of the funnel, admitted through the tap of the latter; this tap is then closed, the lower tap opened, and the stem of the funnel plugged with cotton wool.

The gas formed by the organisms collects under pressure in the funnel, and may be transferred to a gas burette for examination.

W. P. S.

The Influence of Dicyanodiamide on the Growth of various Micro-organisms. LUISE MOLLER (*Biochem. Zeitsch.*, 1918, **88**, 85—96).—Experiments were carried out with various wild yeasts, moulds, and bacteria, and these indicate that dicyanodiamide has no advantages as a sole source of nitrogen for organisms; on the contrary, it exerts a deleterious action on their growths.

S. B. S.

A Study of the Antiseptic Properties of certain Organic Compounds. I. J. KLIGLER (*J. Exp. Med.*, 1918, **27**, 463—478; from *Physiol. Abstr.*, 1918, **3**, 270—271).—An examination of the antiseptic properties of a number of organic compounds, including dyes of the triphenylmethane series.

S. B. S.

The Formation of Ferments. VII. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **88**, 35—42. Compare this vol., i, 328). —The conditions for the formation of the catalase of *Proteus* were investigated. Whilst leucine is essential for the formation of urease by this species of bacteria, this is not the case for formation of the catalase. Other amino-acids, such as aspartic acid and alanine, can be employed, and a considerable development of this ferment takes place in a medium containing, besides the essential inorganic salts and one of these amino-acids, sodium lactate. The catalase acts after the bacteria have been killed (that is, in the presence of toluene). If inactivated by not too large quantities of mercuric chloride and too long a period of contact with this substance, its activity can be restored by treatment with potassium cyanide.

S. B. S.

The General Relationship of Aldehydes to Alcoholic Fermentation. The Co-ferment of Yeast. CARL NEUBERG (*Biochem. Zeitsch.*, 1918, **88**, 145—204).—The author gives detailed experiments which confirm his previous statement that aldehydes generally accelerate the alcoholic fermentation by yeasts of dextrose and mannose. His experiments include a series of fatty aldehydes from formaldehyde up to decaldehyde, chloral hydrate, hydroxyaldehydes (aldol, acetopropionaldol), unsaturated aldehydes (citronellal and citral), aromatic aldehydes (benzaldehyde, *p-iso*propylbenzaldehyde, phenylacetaldehyde), aromatic hydroxy-aldehydes and their ethers (salicylaldehyde, *p*-hydroxybenz-aldehyde, anisaldehyde, piperonal, and vanillin, which is the only aldehyde which failed to give acceleration), the unsaturated aromatic aldehyde, cinnamaldehyde, cyclic aldehydes (furfur-aldehyde and *cyclo*citral), dialdehydes (glyoxal, *iso*phthalaldehyde, terephthalaldehyde), keto-aldehydes (methylglyoxal and phenyl-glyoxal), and aldehyde-acids. The author also confirms his former statement that a mixture of keto-acids with potassium phosphate acts as a co-ferment. He suggests that certain differences in results

on this point obtained by Harden (A., 1917, i, 501) may be due to the fact that the yeast preparations employed by the latter were not quite free from co-ferments. S. B. S.

Chromogenic Yeasts. New Biological Reaction for Iron. M. W. BEYERINCK (*Arch. Néerland. Physiol.*, 1918, **2**, 609—615). —Several yeasts containing lactase have the property of secreting under favourable conditions a colourless chromogen which, in the presence of a salt of iron and atmospheric oxygen, is converted into a red pigment. The "fat" yeast, *S. pulcherrimus*, which is characterised by its power of forming fat, does not contain lactase, but it nevertheless forms the above colourless chromogen and red pigment more readily and abundantly than any of the other yeasts. Since it occurs frequently on grapes and in heather honey, and can thus be easily obtained, it has been employed by the author for the preparation and examination of the chromogenic substance. If the yeast is grown on an iron-free medium, pigmentation does not occur. On adding a trace of an iron salt and exposing to air, the red coloration gradually appears. Inoculation of the yeast into a medium containing as little as 10 mg. of iron citrate in 100 c.c. is sufficient to cause the developing yeast cells to become surrounded with a pigmented halo, whilst with larger quantities of iron the cells themselves become red.

The pigment has acidic properties, forming colourless salts with strong bases, which when acidified again produce red solutions. It is a stable substance; its solution in dilute sulphuric acid may be boiled without the occurrence of any decomposition. It does not appear to belong to the anthocyanin or the carotinoid group of pigments. H. W. B.

Anæsthesia and Respiration. A. R. C. HAAS (*Science*, 1917, N.S., **46**, 462—464).—Using a method previously described (compare A., 1917, i, 433) for the estimation of small quantities of carbon dioxide in solution, the author finds that when *Laminaria* is exposed in sea-water to the action of anæsthetics, in sufficient concentration to produce a measurable effect, there is an increase in respiration. This may be followed by a decrease if the reagent is sufficiently toxic. No decrease is observed with low concentrations which are not toxic. W. G.

Photosynthesis. W. J. V. OSTERHOUT (*Amer. J. Bot.*, 1918, **5**, 105—111).—For the demonstration of photosynthesis, an apparatus is described which permits of the removal, at intervals, of satisfactory samples of the gases by which the leaf is surrounded, of the stirring and mixing of the gases when necessary, and of the analysis of the gases by a simple method which is sufficiently accurate for ordinary purposes. The apparatus is figured in the original. W. G.

A Simple Method of Measuring Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS (*Science*, 1918, *N.S.*, **47**, 420—422). —Minute amounts of photosynthesis can be accurately measured

by placing aquatic plants, such as *Ulva, Spirogyra, Hydrodictyon,* and *Potamogeton,* in solutions containing hydrogen carbonates with a little phenolphthalein, and observing the change in the colour of the indicator on exposure to sunlight. The method can be used for quantitative investigations or for demonstration purposes.   W. G.

Methods of Studying Permeability of Protoplasm to Salts. S. C. BROOKS (*Bot. Gaz.*, 1917, **64,** 230—249).—A general discussion of the methods commonly used in the study of permeability, from which the steps most essential to further progress in the solution of the problem are considered to be: (1) an analysis of the various disturbing factors in the methods involving chemical estimations and the satisfactory interpretation of the results obtained by these methods; (2) a similar analysis of the methods depending on turgor, with special reference to the possible effect of exosmosis; (3) the establishment of methods determining progressive changes in permeability without the disadvantages attaching to the methods at present in use. The author considers that his diffusion method (compare following abstract) answers these requirements.   W. G.

A New Method of Studying Permeability. S. C. BROOKS (*Bot. Gaz.*, 1917, **64,** 306—317).—The method described depends on the diffusion of salts or other substances through a diaphragm of living tissue. Two cells are prepared of glass tubing 18 mm. in diameter, one being 2·5 cm. and the other 4 cm. in length, the ends being ground flat. Between these two edges is placed the tissue, and the cells are rapidly filled with the necessary solutions in turn, and the apparatus set up vertically, the longer cell being at the bottom and closed by a rubber tube and clip, and the upper cell covered to prevent loss by evaporation. The permeability, as shown by the rate of passage of salts through the diaphragm, is measured by determining the changes in electrical conductivity of the two solutions. Where dead tissue is required for experiments on the permeability of the intercellular substance, living disks are exposed to an atmosphere saturated with chloroform vapour for sixteen to twenty-four hours. The results obtained with disks of *Laminaria Agardhii* indicate that the protoplasm of this kelp is normally permeable to the salts of sea-water. Sodium salts cause an increase of permeability, which culminates in death. Calcium and lanthanum salts cause a decrease in permeability, followed by an increase, which culminates in the death of the tissue. W. G.

Antagonism and Permeability. W. J. V. OSTERHOUT (*Science*, 1917, *N.S.*, **45,** 97—103).—Experiments show that all substances which affect permeability may be divided into two groups: (1) those which act like sodium chloride, (2) those which act like calcium chloride (compare Brooks preceding abstracts). It was further found that substances which behave like sodium chloride

with respect to antagonism, in experiments on growth, behave like sodium chloride in their effect on permeability, and similarly for the second group. There is thus a striking parallel between effects on permeability and antagonistic effects in growth, and all solutions which permit normal growth also preserve normal permeability. The author discusses possible theoretical explanations of these facts and gives experimental data in support of his theory.   W. G.

Does the Temperature-coefficient of Permeability indicate that it is Chemical in Nature ? W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, **63**, 317—320).—The results of Stiles and Jörgensen (compare A., 1916, i, 108) indicate that permeability is chemical rather than physical in nature. From a brief, critical survey of their work, and taking into account his own work on the temperature-coefficient of permeability (compare *Biochem. Zeitsch.*, 1914, **67**, 272), the author does not accept the view that permeability is chemical in nature.   W. G.

Similarity in the Effects of Potassium Cyanide and of Ether. W. J. V. OSTERHOUT (*Bot. Gaz.*, 1917, **63**, 77—80).—When potassium cyanide is added to sea-water in which are tissues of *Laminaria Agardhii*, it first causes a temporary decrease in permeability, thus resembling, in this respect, anæsthetics such as ether, chloroform, and alcohol, but the concentrations of potassium cyanide necessary to produce a decrease of permeability are very much smaller than the corresponding concentrations of the latter substances.   W. G.

The Antagonistic Action of Salts. L. W. H. VAN OYEN (*Biochem. Zeitsch.*, 1918, **87**, 418—424).—A preliminary account of attempts to correlate physical properties of salts in solution with their biological action. It is shown that chlorine is adsorbed less by various adsorbents from solutions containing sodium, potassium, and calcium chlorides than from a solution of sodium chloride alone. The proportions of the various cations in the experiments were those used by Osterhout in his biological experiments. Experiments are also described on diffusion of chlorine through a dialyser from solutions of sodium chloride alone or mixed with potassium and calcium chlorides.   S. B. S.

The Reduction of Carbon Dioxide by Hydrogen Peroxide as the Basis of Assimilation by Plants. HANS WISLICENUS (*Ber.*, 1918, **51**, 942—965).—The reduction of carbon dioxide to formic acid, but not to formaldehyde, has been achieved by many chemists, among whom Bredig and Carter have been most successful from a practical point of view (A., 1914, i, 377). It is recognised, however, that there is no resemblance between the powerful agents employed in the laboratory and the forces at the disposal of the green plant. One agent which is always at hand in nature is hydrogen peroxide, and this is to be regarded as the substance which causes the transformation of carbonic acid into formic acid

(compare Kleinstück, this vol., ii, 107). With the exception of the per-acids, carbonic acid is the only carboxylic acid the anhydride and charged or uncharged anions of which have a peroxidic structure, and the mechanism of the formation of oxygen and formic acid is therefore a mutual deoxidation of two peroxides, a reaction which requires no expenditure of energy.

A series of experiments is described which shows that oxygen and formic acid are actually produced when carbonates are left with hydrogen peroxide, the best results being obtained with a saturated solution of potassium hydrogen carbonate and a 10% solution of hydrogen peroxide. The reaction in this case is represented thus:

$$H_2O_2 + \frac{H}{K}\begin{bmatrix} O \\ | \\ O \end{bmatrix} CO = H_2O + O_2 + H \cdot CO_2K.$$
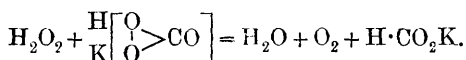
According to the above view, the process is one which concerns anions, and therefore a formate should be produced around the anode during the electrolysis of a carbonate or hydrogen carbonate, for the peroxidic anion will be in contact with hydroxyl ions. This also has been proved experimentally, and it may be possible to find the most suitable conditions of voltage and amperage to study this anodic, peroxidic, "round-about reduction," as it is called, more thoroughly.

The second stage in the assimilation of carbon dioxide is the further reduction to formaldehyde. This requires energy (light), a special catalyst (chlorophyll), and other factors, and is altogether more difficult of achievement than the first step.   J. C. W.

Influence of certain Organic Substances on the Development of Plants. II. G. Ciamician and C. Ravenna (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 38—42).—Further experiments (A., 1917, i, 244, 681) have been made on the influence on beans, maize, beetroot, tobacco and lupin seeds, and plants of mandelonitrile, benzyl and salicyl alcohols (saligenin); potassium benzoate and salicylate; vanillin, eugenol, and tannin; alanine and asparagine; the potassium derivatives of uric acid and xanthine in comparison with caffeine; pyridine and piperidine in comparison with nicotine, and also quinine, strychnine, and morphine. In the germination experiments, use has been made also of cocaine, atropine, and oil of mustard; galvanised iron germinators were used, the seeds being placed on cotton, covered with filter paper, and moistened with 0·1% solutions of the substances mentioned.

The antithetic relations of mandelonitrile and strychnine are confirmed, and so also is the conclusion that the alkaloids in plants possess some unknown but very definite function, which may be that of vegetable hormones. Just as is the case in animals with which the adrenaline of the suprarenal glands is produced from tyrosine, so different species of plants would transform their original indifferent waste products so as to render them fitted for the specific functions they are to serve.   T. H. P.

Nitrate and Nitrite Assimilation. XIII. Iron and Oxygen as necessary Agents for the Reduction of Alkali Nitrites by Auto-oxidisable Compounds. OSKAR BAUDISCH (*Ber.*, 1918, **51**, 793—805. Compare A., 1916, i, 699—702; 1917, i, 434).— In the last communication, the important discovery was recorded that when solutions of aldoses or ketoses are boiled with ferrous sulphate and sodium carbonate, dark reddish-violet solutions are obtained, containing iron in "internally-complex" union, which have specific reducing properties. For example, alkali nitrites may be reduced to nitric oxide and ammonia, which is again supposed to involve the hypothetical acid, NOH, as an intermediate stage. It is now shown that the activity of the reducing solution is unaffected by oxygen, which may be freely admitted while the nitrite is being boiled with the agent without preventing the reduction, and that, furthermore, if formaldehyde is added to the mixture, the distillate contains hydroxamic acid, produced according to the equation $CH_2O + NOH = OH \cdot CH \colon N \cdot OH$.

It is further demonstrated that pentoses, dihydroxyacetone, glycollaldehyde, lævulose, and maltose, in addition to the original dextrose and lactose, have the power of forming complex iron compounds which can reduce nitrites, but not nitrates, or nitrobenzene to aniline. It is not necessary, however, to wait until the iron complex has been made from the carbohydrate; it may be applied in the form of the deep violet-red solution obtained by adding ferric chloride to an alkaline solution of catechol-*o*-carboxylic acid. Using the iron in this form, it may be demonstrated that glycerol, glyceric acid, and mannitol cannot reduce nitrobenzene; in other words, only aldoses and ketoses (in this group of compounds) have the property. If the violet catecholcarboxylic acid complex is boiled with dextrose, the solution becomes more brownish-red, showing that the metal is transferred to the sugar molecule.

Developing the subject further, the author has found that not only aldoses and ketoses, but such compounds as catechol, quinol, pyrogallol, gallic acid, phloroglucinol, quercetin (representing yellow plant pigments), and chrysarobin (representing the anthranols) can reduce nitrites if internally complex iron is present. Now, all these compounds are known to be auto-oxidisable, that is, they take up oxygen and in the presence of water produce hydrogen peroxide (compare Bach, A., 1897, ii, 401; Engler, 1897—1901; Manchot, A., 1900, i, 300). This is an important consideration, for these compounds will only reduce nitrites in the presence of oxygen. For example, if a solution of 1:8-dihydroxyanthranol (used in cases of psoriasis under the name "cignolin") is boiled with sodium carbonate, a few drops of ferric chloride, and sodium nitrite, no ammonia or nitric oxide whatever passes over in the distillate if the apparatus is first filled with pure nitrogen, but reduction takes place as soon as oxygen is admitted, and ceases again if this gas is excluded once more. Only the sugars are capable of causing the reduction in the absence of oxygen, but

these can provide the necessary oxygen from their own molecules, as Wieland has indicated (A., 1913, i, 1304).

Special experiments emphasise the point again that traces of iron in the "complex" condition must be present. Manganese and copper are without influence. Some of the above polyhydroxyl compounds, like the sugars, can make complexes from iron hydroxides, but not all of them. Phloroglucinol is unable so to "mask" ferric hydroxide, but does make a complex if potassium ferricyanide is provided.

Some theoretical considerations as to these phenomena are offered, and the bearing of them on biochemical processes is mentioned. Particularly important is the power of these auto-oxidisable compounds to bring about oxidations on the one hand (for example, methyl alcohol to formaldehyde) and reductions of nitrites, in the presence of iron complexes, on the other. It is well known that such compounds are widely dispersed in nature—phloroglucinol in many green plants, catechol and quinol in leaf buds, gallic acid, tannin, chrysarobin, yellow pigments, and anthocyanins. It has been shown, furthermore, that the secretion of tanning substances increases when plants are cultivated under less favourable conditions, such as in the cold or dark. In the animal body, also, phenolic compounds with adjacent hydroxyl groups play an important part; for example, adrenaline, and the pigment-forming amino-acid, 3:4-dihydroxyphenylalanine (Bloch, A., 1917, i, 675). Likewise in therapeutics, especially in dermatology, such phenols exert effects that strong reducing or oxidising agents alone are incapable of.   J. C. W.

The Distribution of the Aluminium Ion in Plants. JULIUS STOKLASA [with J. SEBOR, W. ZDOBNICKÝ, F. TYMICH, O. HORÁK, A. NĚMEC, and J. CWACH] (*Biochem. Zeitsch.*, 1918, **88**, 292—322).—Aluminium is widely distributed in plants. A large number of analyses are tabulated. The xerophytes contain only small amounts of aluminium, whereas the hydrophytes and hygrophilic plants contain relatively large quantities. The mesophytes when growing on dry soils are very poor in aluminium, but contain an appreciable quantity when growing on marshy ground.

S. B. S.

Direct Influence of the Sap elaborated by the Wild on the Cultivated [Plant], and the Action that Acid Solutions, Directly Absorbed, exert on the Plant. C. CAMPBELL (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 57—61).—According to Comes, the greater resistance normally shown by wild plants when compared with cultivated ones is due to the greater acidity of the juices of the former. In order to obtain information bearing on this hypothesis, the author has carried out preliminary experiments to ascertain: (1) the influence exerted on a cultivated stock by a wild

graft, and (2) the effect on plants of the direct absorption of acid solutions.   T. H. P.

Occurrence of Carotin in Oil and Vegetables. AUGUSTUS H. GILL (*J. Ind. Eng. Chem.*, 1918, **10**, 612—614).—Carotin was found to be present in maize, squash, orange-peel, flax seed, mustard seed, black sesame seed, butter, tallow, palm oil, and grass, but not in rape seed, white sunflower seed, turnip, safflower, cotton seed, or turmeric.   W. P. S.

Chemical Investigations on Elaphomyces hirtus. G. ISSOGLIÒ (*Gazzetta*, 1917, **47**, ii, 31—48).—Analysis of *Elaphomyces hirtus* shows that it contains a *micosterol*, $C_{30}H_{54}O_3$, crystallising in silky, white needles, m. p. 265°; traces of unidentified alkaloids; mannitol; micoinulin, which gives no coloration with iodine and does not reduce Fehling's solution; para*iso*dextran, extractable by dilute alkali solution and coloured reddish-brown by iodine; fungin, containing 2·28% of nitrogen. The spores contain a brown pigment with 5% of nitrogen.   T. H. P.

Carbohydrates in Mulberry Leaves. SŌJIRŌ KAWASE (*Journ. Tokyo Chem. Soc.*, 1918, **39**, 245—294).—The carbohydrates in mulberry leaves are dextrose, lævulose, sucrose, starch, dextrin, araban, galactan, and cellulose. Of these, cellulose occurs in largest amount, next comes a viscous substance consisting of araban and galactan, whilst starch is present in relatively small amount. The nutriment for the silkworm is therefore not starch as is generally supposed. The viscous substance in the leaves does not contain albuminous matter. The changes in the amounts of carbohydrates in the leaves during the development of the plant, or according to the time of gathering the leaves, or during the drying after gathering were determined, and are discussed from the physiological point of view.   S. H.

Biochemistry of Sea Weeds. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1918, **101**, 236—247. Compare A., 1915, i, 931). —Various kinds of algæ have been examined for the presence of soluble carbohydrates and laminarin. Of eight species of brown algæ, two, *Desmarestia aculeata* and *D. viridis*, contained laminarin, whilst in all the percentage of soluble carbohydrates was small. Four species of *Floridex* were found to contain trehalose, but not mannitol. Of the *Chlorophyzex* investigated, *Cladophora rupestris* contained 15% of soluble carbohydrates, including saccharose, and a lævorotatory polysaccharide resembling inulin.   H. W. B.

Isolation and Identification of Stachydrin from Lucerne Hay. H. STEENBOCK (*J. Biol. Chem.*, 1918, **35**, 1—13. Compare A., 1917, i, 439).—A full account of work previously published.
                                                               H. W. B.

Organic Chemistry.

Two New Trihydric Alcohols. MORITZ KOHN and VIKTOR NEUSTÄDTER (*Monatsh.*, 1918, **39**, 293—298).—It has already been found possible (Kohn, A., 1914, i, 74) by the action of magnesium methyl iodide on the lactone of $\alpha\gamma$-dihydroxy-$\alpha\gamma$-dimethyl-*n*-valeric acid to obtain $\beta\gamma\epsilon$-trihydroxy-$\beta\gamma\epsilon$-trimethyl-*n*-hexane. Form*iso*-butyraldol, by successive treatment with sodium hydrogen sulphite and potassium cyanide (compare Glaser, A., 1904, i, 284), can be converted into the lactone of $\alpha\gamma$-dihydroxy-$\beta\beta$-dimethyl-*n*-butyric acid, b. p. 118—120°/12 mm., 237—241°/ord. pressure, which reacts with magnesium methyl iodide in a similar manner to the above compound, forming $\alpha\gamma\delta$-*trihydroxy*-$\beta\beta\delta$-*trimethyl*-n-*pentane*, $OH \cdot CH_2 \cdot CMe_2 \cdot CH(OH) \cdot CMe_2 \cdot OH$, b. p. 152—155°/12 mm., 256—262°/ord. pressure, which slowly solidifies to a crystalline mass, m. p. 68—70°. When heated with 33% sulphuric acid, this compound yields a *substance*, $C_8H_{16}O_2$, b. p. 187—192°, of camphor-like odour, probably 4-*hydroxy*-3:3:5:5-*tetramethyltetrahydro-furan*, $\begin{matrix} CH_2 \cdot CMe_2 \\ | \\ O \text{---} CMe_2 \end{matrix} > CH \cdot OH$. The action of magnesium phenyl bromide on the lactone proceeds in an analogous manner, and yields $\alpha\gamma\delta$-*trihydroxy*-$\delta\delta$-*diphenyl*-$\beta\beta$-*dimethyl* - n - *butane*, microscopic needles, m. p. 130—133°. D. F. T.

Action of Phosphorus Trichloride on Aliphatic Alcohols. T. MILOBENDZKI and A. SACHNOWSKI (*Chemik Polski*, 1917, **15**, 34—37; from *Chem. Zentr.*, 1918, i, 911—912).—The action of phosphorus trichloride on any alcohol results in the immediate formation of the normal ester of phosphorous acid, which is decomposed by the liberated hydrogen chloride into acid ester and alkyl chloride, $PCl_3 + 3R \cdot OH = P(OR)_3 + 3HCl \longrightarrow OH \cdot P(OR)_2 + RCl \longrightarrow OR \cdot P(OH)_2 \longrightarrow P(OH)_3 + RCl$. The decomposition of alkyl phosphites into phosphorous acid and unsaturated hydrocarbons is a secondary reaction which occurs most readily with esters derived from tertiary alcohols (even at low temperature and under diminished pressure).

The authors have demonstrated that the reaction for the diagnosis of isomeric alcohols (action of dry hydrogen chloride on the alkyl phosphites) proceeds quantitatively and is not merely a qualitative test.

For the preparation of normal esters, the following method is recommended. The mixture of alcohol (3 mols.) and pyridine (3 mols.) is largely diluted with ether, and phosphorus trichloride (1 mol.) is added drop by drop to the ice-cold mixture. The precipitated pyridine hydrochloride is filtered. The following yields were obtained: trimethyl phosphite, b. p. 110—111·5°/745 mm.

(crude product, 70%; pure substance, 42·5%); triethyl phosphate, b. p. 155—156°/740 mm. (73%); tri-*n*-propyl phosphite, b. p. 82—84°/10 mm. (89%); *tri*-n-*butyl phosphite*, b. p. 122—123°/12 mm., D_0^{20} 0·92547, D_4^{20} 0·92530, D_{20}^{20} 0·92692 (96%).

Dialkyl phosphites are prepared by a similar method, except that only two molecules of pyridine are used for each molecule of phosphorus trichloride. The details are as follows: dimethyl hydrogen phosphite, b. p. 56—58°/10 mm. (ca. 35%); diethyl hydrogen phosphite, b. p. 72—73°/9 mm. (85%); di-*n*-propyl hydrogen phosphite, b. p. 91—92°/10 mm. (96%); *di*-n-*butyl hydrogen phosphite*, b. p. 124—125°/12 mm., D_0^{20} 0·99516, D_4^{20} 0·99503, D_{20}^{20} 0·99697 (97%).

Attempts have been made to prepare mono-alkyl phosphites by the action of phosphorus trichloride on the alcohols saturated with hydrogen chloride; a relationship between the product of the reaction and the degree of saturation of the alcohol has been traced, but this section of the work has not been completed.

The reaction between phosphorus trichloride and trimethylcarbinol has been similarly investigated. The formation of unsaturated hydrocarbons and of trimethylcarbinyl chloride is not observed during the action when three molecules of pyridine are used for each molecule of phosphorus chloride. The product, the composition of which corresponded fairly accurately with that required for $(C_4H_9O)_3P$, could not be distilled without decomposition, whereby di*iso*butylene, b. p. 102—103°/758 mm., tri*iso*-*butylene*, b. p. 178—180°/752 mm., together with unchanged tributyl phosphite, were obtained. Di-*tert.*-butyl hydrogen phosphite is still more readily decomposed, yielding at 38° (30 mm.) di- and tri-*iso*butylene.   H. W.

Action of Water on Dialkyl Phosphites. T. MILOBENDZKI and A. SACHNOWSKI (*Chemik Polski*, 1917, **15**, 48—55; from *Chem. Zentr.*, 1918, i, 912—913. Compare Milobendzki, A., 1912, i, 155).—The stability of dialkyl phosphites in aqueous solution and their electrical conductivity have been investigated. Hydrolysis of the esters, $OH \cdot P(OR)_2$, with alkali or barium hydroxide in solutions which are not below $0 \cdot 05N$ proceeds too rapidly for accurate measurement. The hydrolysis of the esters proceeds slowly in aqueous solution at 25°; measurements have been made for diethyl hydrogen phosphite and dipropyl hydrogen phosphite, for full details of which the original paper must be consulted. The velocity of hydrolysis is very high at first, then decreases, subsequently increases, and finally sinks.

The dialkyl hydrogen phosphites behave as neutral substances. They do not combine with ammonia even when nascent; their aqueous solutions are neutral to indicators. The conductivity of the aqueous solutions is small—about ten times that of the water. The electrical conductivity of an equimolecular mixture of dipropyl hydrogen phosphite and silver nitrate is less than the sum of their conductivities. In the first thirty to forty minutes, no reaction

appears to occur; subsequently, the silver salt, $OAg \cdot P(OPr)_2$, slowly commences to separate, but precipitation is not complete after forty hours. The silver salt is stable beneath the aqueous solution in the dark and does not begin to decompose for about forty hours. H. W.

Salts of Alkyl Hydrogen Phosphites. T. MILOBENDZKI and MARIE SZWEJKOWSKA (*Chemik Polski*, 1917, **15**, 56—65; from *Chem. Zentr.*, 1918, i, 913—914).—Barium monoalkylphosphites are prepared by the neutralisation of monoalkylphosphorous acids or the hydrolysis of dialkyl hydrogen phosphites. *Barium ethyl hydrogen phosphite*, $Ba[O \cdot P(OEt) \cdot OH]_2$, forms hygroscopic crystals; it is completely hydrolysed in warm aqueous solution. *Barium* iso*propyl hydrogen phosphite* is similar. *Ferric propyl hydrogen phosphite*, obtained by the action of ferric hydroxide on an excess of the ester in concentrated aqueous solution or by precipitation of the solution of the barium salt by ferric chloride, is very sparingly soluble in water. It is very slowly attacked by ammonia, rather more rapidly by dilute acids, but is only slowly soluble even in fuming hydrochloric acid. *Ferric* iso*propyl hydrogen phosphite* resembles the *n*-propyl salt. The ferric *iso*butyl and *iso*amyl hydrogen phosphites are similarly prepared. The monomethyl and monoethyl phosphites could not be obtained by precipitation. Cuprous dialkyl phosphites, $(OR)_2P \cdot OCu$, are obtained when cuprous oxide acts on an aqueous solution of excess of the ester in closed vessels. The reaction, $(OR)_2P \cdot OH + CuOH \longrightarrow (OR)_2P \cdot OCu + H_2O$, proceeds slowly and is complete in five days; simultaneously, the white cuprous salt is slowly oxidised to the blue cupric salt, copper being precipitated. Purification is effected by pouring the product into water, when the copper and copper oxide sink, the cupric salt passes into solution, and the cuprous salt collects on the sides of the vessel. The dry salts are stable. The *cuprous* salts of diethyl, dipropyl, and di*iso*propyl hydrogen phosphites are described. The silver salts of the dialkyl phosphites are obtained by the cautious addition of alkali or of a solution of a readily hydrolysed salt to an aqueous solution of equivalent quantities of silver nitrate and the requisite ester, or, preferably, by treatment of the solution of the dialkyl phosphite with ammoniacal silver nitrate and immediate neutralisation of the ammonia with nitric acid. The ester suffers a certain amount of hydrolysis, which is less marked when the second of the above methods is adopted. The silver salts are sparingly soluble in water, soluble in ammonia and alkalis. The diethyl and dipropyl salts have been particularly investigated. H. W.

Constitution of Dioxalomalonic Ester and other Acylated Esters. KARL VON AUWERS and ELISABETH AUFFENBERG (*Ber.*, 1918, **51**, 1087—1106. Compare A., 1917, i, 627).—The discovery that the so-called "ethyl diacetylmalonate," $CAc_2(CO_2Et)_2$, is really to be regarded as ethyl β-acetoxyethylidenemalonate,

$OAc \cdot CMe \colon C(CO_2Et)_2$, raises the question whether genuine diacyl-malonic esters can be obtained at all, and whether they may not perhaps be present in small quantities in specimens of the isomeric esters. In the case of the "dioxalomalonates," Scholl and Egerer (A., 1913, i, 588) have already considered the two alternatives, analogous with the above, and decided on a formula of the true diacylmalonate type, thus, $(CO_2R \cdot CO)_2C(CO_2R)_2$, and not
$$CO_2R \cdot CO_2 \cdot C(CO_2R) \colon C(CO_2R)_2.$$
Their decision depended chiefly on the facts that the compounds in question did not immediately reduce alkaline permanganate and gave carbon monoxide on heating, but it is now shown that these arguments have no weight and that the optical properties of the esters agree with the alternative formula. The refractions and dispersions are abnormally high and agree with the enolic structure rather than with the methanetetracarboxylate type. Furthermore, "ethyl oxalomalonate" is found by titration to exist to the extent of 60% in the enolic form, $CO_2Et \cdot C(OH) \colon C(CO_2Et)_2$.
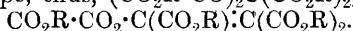
These results support the opinion, often expressed by Claisen, that compounds of the type $C(CO \cdot)_4$ do not, generally speaking, exist, but tend to undergo rearrangement into isomerides in which at least one carbonyl group is attached to oxygen. There are exceptions to this generalisation, however. Scholl and Egerer's methanetetracarboxylates and acetylmethanetricarboxylates have optical properties which agree with the type $C(CO \cdot)_4$. The latter esters are obtained by acetylating the sodiomethanetricarboxylates, and it appears that compounds of the above type can only be obtained from methanetricarboxylates, for if the alternative procedure is adopted, namely, acetylation of malonic esters, followed by treatment with chloroformic esters, the products are the enolic isomerides.

With the co-operation of Scholl and Egerer, the optical properties of pure specimens of their methanecarboxylates have been investigated. Ethyl methanetricarboxylate has b. p. 139°/14 mm., m. p. 27–29°, $D_4^{1 \cdot 2}$ 1·1091, n_a 1·42628, n_D 1·42828, n_β 1·43392, n_γ 1·43838, at 14·2°, $E\Sigma_a + 0\cdot24$, $E\Sigma_D + 0\cdot21$, $E\Sigma_\beta - \Sigma_a + 2\%$, $E\Sigma_\gamma - \Sigma_a + 1\%$. Ethyl methanetetracarboxylate has b. p. 185°/18 mm, D_D^{17} 1·1357, n_a 1·43300, n_D 1·43563, n_β 1·44085, n_γ 1·44561, at 17°, $E\Sigma_a$ 0·36, $E\Sigma_D$ 0·36, $E\Sigma_\beta - \Sigma_a$ 3%, $E\Sigma_\gamma - \Sigma_a$ 4%. Dimethyl diethyl methanetetra-carboxylate has $D_4^{17 \cdot 2}$ 1·1828, n_a 1·43098, n_D 1·43327, n_β 1·43891, n_γ 1·44350, at 17·2°, $E\Sigma_a$ 0·39, $E\Sigma_D$ 0·40, $E\Sigma_\beta - \Sigma_a$ 5%, $E\Sigma_\gamma - \Sigma_a$ 2%. Ethyl acetylmethanetricarboxylate, $CAc(CO_2Et)_3$, has b. p. 263°/ atm., 154°/11 mm., $D_4^{13 \cdot 1}$ 1·1277, n_a 1·43354, n_D 1·43562, n_β 1·44158, n_γ 1·44638, at 13·1, $E\Sigma_a$ 0·37, $E\Sigma_D$ 0·35, $E\Sigma_\beta - \Sigma_a$ 5%, $E\Sigma_\gamma - \Sigma_a$ 4%, and is decomposed by phenylhydrazine and aniline in the cold, phenylacet-hydrazide and acetanilide being deposited.

These data show that the refraction and dispersion of the tetra-carboxylates are somewhat abnormal, which might be expected of compounds with so many carbonyl groups in close proximity, but the abnormality is by no means of the same order as that revealed by enolic compounds. For example, *ethyl β-ethylcarbonatoethyl-*

phenylhydrazine or semicarbazide. The dibenzoyl *compound* has
m. p. 112—113°.   H. W.

Preparation of Alkylselenocarbamides. CHEMISCHE FABRIK
VON HEYDEN (D.R.-P., 305262; from *Chem. Zentr.*, 1918, i, 976).
—Alkylselenocarbamides are prepared by the action of hydrogen
selenide on alkylcyanamides. The substances have a therapeutic
value in the treatment of cancerous disease, and serve as inter-
mediate products in the production of the more stable alkyl haloid
additive compounds. *Allylselenocarbamide* forms almost colourless
needles. m. p. 93°, which become superficially red owing to the
separation of selenium; it unites with bromine and iodine and
reduces alkaline permanganate. It is very sensitive to air and
light. The *mercury* and *lead* salts eliminate selenium. *Ethyl-
selenocarbamide* forms colourless needles, m. p. ca. 125°.
                                                            H. W.

Preparation of Derivatives of Alkylselenocarbamides.
CHEMISCHE FABRIK VON HEYDEN (D.R.-P., 305263; from *Chem.
Zentr.*, 1918, i, 976).—The alkylselenocarbamides combine readily
with alkyl haloids to yield compounds in which the selenium is
more firmly combined than in the parent selenocarbamides; they
are more stable towards light and more soluble in water. Their
composition is probably expressed by the formula
$$Alk \cdot NH \cdot C(NH_2) : SeI \cdot Alk.$$
The *compound* formed from allylselenocarbamide and ethyl iodide
forms white leaflets. m. p. about 100°; the iodine is precipitated
as silver iodide by silver nitrate. The selenium is not precipitated
as lead or mercury selenide by lead or mercury salts, as in the case
of allylselenocarbamide. The *compound* from ethylselenocarb-
amide and allyl bromide has m. p. 115°.   H. W.
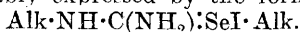
Acetyl Cyanide. ROLAND SCHOLL [with JOSEF ADLER] (*Monatsh.*,
1918, **39**, 240).—Acetyl cyanide is conveniently prepared by boil-
ing a solution of oximinoacetone in carbon disulphide with a little
more than the theoretical quantity of phosphorus pentoxide for
three-quarters of an hour and then distilling; the yield is
approximately 40%.   D. F. T.

Organic Chemical Reagents. I. Dimethylglyoxime.
ROGER ADAMS and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1918, **40**,
1281—1289).—Methods of manufacturing the less common organic
chemicals are being thoroughly worked out at the University of
Illinois, and full details of the processes will be published with the
object of inducing manufacturers to take up the production of the
more useful of such reagents.
     The present communication deals with the manufacture of
dimethylglyoxime. This substance can be made by several
methods, but the only one that is easily and cheaply adapted for
large scale production is that of Gandurin (A., 1908, i, 400). The
paper describes (1) the preparation of hydroxylamine sulphate and

(2) of amyl nitrite, (3) methyl ethyl ketone, (4) the preparation of its oximino-derivative and (5) of dimethylglyoxime, (6) the puri-fication of coloured dimethylglyoxime, and (7) the recrystallisation of dimethylglyoxime.

The removal of coloured impurities in dimethylglyoxime is effected by treating its saturated solution in 8% sodium hydroxide solution with an excess of concentrated ammonium chloride solu-tion; the colourless precipitate of dimethylglyoxime is filtered immediately. The process is repeated if necessary.   C. S.

Action of Magnesium and Zinc on Dichloromethylarsine.

ENRIQUE V. ZAPPI (*Bull. Soc. chim.*, 1918, [iv], **23**, 322—324).— In the presence of anhydrous ether, magnesium does not act on dichloromethylarsine, but in the presence of water the two react violently, giving methylarsine, hydrogen, and methane, methyl-arsenide, $(CH_3As)_x$, being precipitated and magnesium chloride left in solution. Zinc produces a similar decomposition.   W. G.

Hydrocarbo-bases and a Study of Organic Derivatives of Mercury and of Lead.

LAUDER W. JONES and LOUIS WERNER (*J. Amer. Chem. Soc.*, 1918, **40**, 1257—1275).—Hydrides of metals and organo-metallic compounds react with acids and sup-press hydrogen ions; for example, (1) $NaH + HX = NaX + H_2$, (2) $Zn(CH_3)_2 + 2HX = ZnX_2 + 2CH_4$. If this property is sufficient reason for classifying these substances as bases, the former may be termed hydrogen bases and the latter hydrocarbo-bases. When compared with aquo-bases (KOH) and ammono-bases (KNH_2), the striking resemblance in chemical behaviour of these substances towards hydrogen ions seems to demand some factor common to all as the cause of the analogy, and the authors endeavour to find this factor in the theory of the electron conception of valency and Fry's theory of electromers (A., 1911, i, 431). The most obvious explanation of the similar reactivity of these various classes of bases would be to consider all groups combined with the metallic atoms in these compounds negative in the electronic sense. Whilst the organo-metallic compounds resemble aquo-bases and ammono-bases in certain other respects, as, for example, in forming basic salts and in undergoing double decomposition in reactions, they and the hydrogen bases differ from these in one important respect—they are powerful reducing agents. This property is explained by the powerful tendency of negative hydrogen to become positively charged and of negative alkyl groups (or of a carbon atom in them) to lose negative electrons and to assume positive charges.

Mercury diethyl is known to dissociate at about 200° to give mercury and butane. The dissociation, considered electronically, implies that one of the alkyl groups functions negatively and the other positively. $Hg \genfrac{}{}{0pt}{}{-}{+} \genfrac{}{}{0pt}{}{+ Et}{- Et} \rightarrow Hg + Et^- \cdot ^+ Et$. Such groups should therefore exhibit differences in chemical reactivity, and this is

shown to be the case. Oxidation with permanganate removes only one group, R·Hg·OH being formed, and mercury dibenzyl, heated with glacial acetic acid at 160—170°, yields mercury, toluene, and benzyl acetate, together with some dibenzyl. Benzyl mercuriacetate under the same conditions gives only mercury and benzyl acetate, toluene and dibenzyl not being formed. Similar results are obtained with mercury diethyl and mercury di*iso*amyl, mercury, ethane or pentane, and ethyl or *iso*amyl acetate being obtained. Mercury diphenyl and mercury dimethyl give mercury and hydrocarbons, the acetate of the phenol or alcohol not being formed.

Similarly, tetra-alkyl lead compounds react as though three of the alkyl groups were negative and the fourth positive. Thus, lead tetraethyl heated with glacial acetic acid at 250—260° gave lead acetate, ethane (in amount corresponding with three ethyl groups), and ethyl acetate. Results of the same kind were obtained with lead tetramethyl.   C. S.

Dibromopyranthrone and Attempts to Prepare Benzanthrones. ROLAND SCHOLL (*Monatsh.*, 1918, **39**, 231—236).— [With W. NEUBERGER.]—The substance obtained from pyranthrone by the action of bromine at 100° is a *dibromo*-compound, $C_{30}H_{12}O_2Br_2$.

[With W. TRITSCH.]—2-*Iodo*-1-*methylnaphthalene*, $C_{11}H_9I$, pearly leaflets, m. p. 51·5°, prepared from 1-methyl-2-naphthylamine by the diazo-reaction, when heated with finely divided copper at 220—260° undergoes conversion into 1 : 1'-*dimethyl*-2 : 2'-*dinaphthyl*, $C_{22}H_{18}$, colourless needles, m. p. 230°. The corresponding *dibenzyl*-2 : 2'-*dinaphthyl*, $C_{34}H_{26}$, and *di*-p-*chlorobenzyl*-2 : 2'-*dinaphthyl*, $C_{34}H_{24}Cl_2$, obtained by heating benzyl chloride and p-chlorobenzyl chloride, respectively, with 2 : 2'-dinaphthyl in the presence of zinc chloride, were not pure substances.   D. F. T.

2-Methylanthracene. ROLAND SCHOLL [with JOS. LENKO] (*Monatsh.*, 1918, **39**, 237—238).—2-*Methylanthracene*, $C_{15}H_{12}$, m. p. 206—207°, can be obtained by the action of hydriodic acid and phosphorus on 2-methylanthraquinone.   D. F. T.

Derivatives of Fulvene. V. Condensation of Indene with Ketones. JOHANNES THIELE and KARL MERCK (*Annalen*, 1918, **415**, 257—273. Compare A., 1906, i, 569, 571, 586, 639). —The reactivity of the methylene group in *cyclo*pentadiene, indene, and fluorene decreases as the ethylenic linkings of the 5-ring become double linkings in a benzene nucleus. It has already been shown (*loc. cit.*) that *cyclo*pentadiene condenses extraordinarily easily with ketones, whilst fluorene does not condense at all under the influence of alkaline condensing agents. The behaviour of indene has now been examined. It condenses easily with acetone in the presence of methyl-alcoholic potassium hydroxide, yielding, after boiling for two hours, dimethylbenzfulvene (*picrate*, yellow needles, m. p. 115—116°, sintering at 102°), but at the ordinary temperature, after a week, a mixture of this and ωω-*dimethyl*-3-α-

hydroxyisopropylbenzfulvene, $C_6H_4{<}^{C(:CMe_2)-----}_{C(CMe_2 \cdot OH)}{>}CH$, m. p. 97—98°. Dimethylbenzfulvene is not reduced by aluminium amalgam and moist ether, but is smoothly converted into 3-*isopropylindene*, $C_6H_4{<}^{CPr^\beta}_{CH_2}{>}CH$, faintly yellow oil, b. p. about 230° (decomp.) or 113°/15 mm., by sodium and boiling absolute alcohol.

Indene condenses less readily with aromatic ketones than with acetone. By prolonged boiling with acetophenone and alcoholic sodium ethoxide, it yields ω-phenyl-ω-methylbenzfulvene, yellow crystals, m. p. 68—69°, b. p. 178—179°/5 mm., and by similar treatment it condenses with benzophenone to give ωω-diphenylbenzfulvene (Grignard, A., 1911, i, 193). These two substances are reduced by aluminium amalgam and moist ether to 3-*α-phenylethylindene*, $C_6H_4{<}^{C(CHMePh)}_{CH_2-----}{>}CH$, b. p. 161°/5 mm. and 196°/15 mm., and 3-*benzhydrylindene*, colourless crystals, m. p. 113—114°, respectively. The colours of the three preceding benzfulvenes conform to expectation; they are less intensely coloured than the corresponding fulvenes, and are more intensely coloured than the corresponding dibenzfulvenes (fluorene derivatives).

3-*iso*Propylindene condenses smoothly with benzaldehyde and with anisaldehyde in the presence of 27% methyl-alcoholic potassium hydroxide to form, after about twenty-four hours at the ordinary temperature, 1-*benzylidene*-3-iso*propylindene*,

$$C_6H_4{<}^{-----CPr^\beta}_{C(:CHPh)}{>}CH,$$
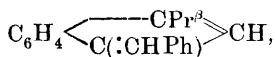
yellow needles, m. p. 105·5°, and the corresponding *methoxybenzylidene* compound, yellow crystals, m. p. 81°, respectively. According to Thiele and Bühner's theory of the oscillating linking (A., 1906, i, 571), the latter of these two compounds ought also to be formed by the condensation of 3-*p*-methoxybenzylindene and acetone, but the product proves to be 3-p-*methoxybenzyl-ωω-dimethylbenzfulvene*, $C_6H_4{<}^{C(:CMe_2)-----}_{C(CH_2 \cdot C_6H_4 \cdot OMe)}{>}CH$, faintly coloured, felted needles, m. p. 83°. This, like other aliphatic fulvenes, is not reduced by aluminium amalgam and moist ether, but is converted by sodium and boiling absolute alcohol into p-*methoxybenzyliso*propylindene, pale yellow oil, b. p. 200°/6 mm., which is also obtained by reducing 1-methoxybenzylidene-3-*iso*propylindene with aluminium amalgam and moist ether. The condensation of benzaldehyde with 3-*p*-methoxybenzylindene and of anisaldehyde with 3-benzylindene (Thiele and Bühner, *loc. cit.*) has therefore been re-examined, and it is now found that the two reactions do not give rise to the same substance under suitable conditions. When the condensations are effected by the prolonged action of methyl-alcoholic potassium hydroxide at the ordinary temperature, the same product, 3-benzyl-1-*p*-methoxybenzylidene-

*a a**

indene, is obtained in both cases, but when the first pair of sub stances is boiled with methyl-alcoholic potassium hydroxide for only two to three minutes, 3-p-*methoxybenzyl*-1-*benzylideneindene*, $C_6H_4 {<} {\stackrel{C(:CHPh)}{C(CH_2 \cdot C_6H_4 \cdot OMe)}} {>} CH$, yellow crystals, m. p. 89—90°, is obtained, which is readily changed to 3-benzyl-1-*p*-methoxybenzyl-ideneindene by the further action of boiling methyl-alcoholic potassium hydroxide.   3-Benzyl-1-*p*-methoxybenzylideneindene is not changed by prolonged boiling with methyl-alcoholic potassium hydroxide, and the same is the case with 3-*p*-methoxybenzyl-ωω-dimethylbenzfulvene and with 1-*p*-methoxybenzylidene-3-*iso*propyl-indene.

3-α-Phenylethylindene (indenylmethylphenylmethane) condenses with anisaldehyde in the presence of methyl-alcoholic potassium hydroxide at the ordinary temperature to form a *benzfulvene*, yellow needles, m. p. 121°, but whether this is ω-phenyl-3-*p*-methoxybenzyl-ω-methylbenzfulvene or 3-α-phenylethyl-1-*p*-meth-oxybenzylideneindene cannot be stated, because the condensation of 3-*p*-methoxybenzylindene and acetophenone to produce the other isomeride could not be effected. 3-Benzhydrylindene and anis-aldehyde similarly condense to form a *benzfulvene*, yellow needles, m. p. 147°, which may be ωω-diphenyl-3-*p*-methoxybenzylbenz-fulvene or 3-benzhydryl-1-*p*-methoxybenzylideneindene.   C. S.

Condensation of Arylated Indenes with Aldehydes.

WALTHER BERNTHSEN (*Annalen*, 1918, **415**, 274—290. Compare Thiele and Merck, preceding abstract).—Since Thiele and Bühner's theory of the oscillating linking has been disproved in the case of the two pairs of isomeric benzfulvenes (*loc. cit.*), it becomes of interest to introduce other aromatic groups in place of phenyl and anisyl, and to ascertain the effects of these on the position of the double linking, that is, the stability of the isomerides. The isomeric pairs are obtained quite simply: (1) indene is condensed with aldehyde *A*, the product is reduced by aluminium amalgam, and the reduction product condensed with aldehyde *B*; (2) indene is condensed with aldehyde *B*, the product reduced, and then con-densed with aldehyde *A*. The condensations in all cases are effected by boiling methyl-alcoholic potassium hydroxide. The aldehydes used are benzaldehyde, *p*-tolualdehyde, *p-iso*propylbenz-aldehyde, *p*-chlorobenzaldehyde, and 2:4-dichlorobenzaldehyde. Anisaldehyde was not employed, because 3-*p*-methoxybenzylindene isomerises during the condensation to anisylidenehydrindene for the most part.

Indene and *p*-chlorobenzaldehyde yield 1-p-*chlorobenzylidene-indene*, $C_6H_4 {<} {\stackrel{C(:CH \cdot C_6H_4Cl)}{CH}} {>} CH$, yellow needles, m. p. 116—117°, which is reduced by moist ether and aluminium amalgam to 3-p-*chlorobenzylindene*, colourless crystals, m. p. 71—73°. Indene and 2:4-dichlorobenzaldehyde yield a mixture of 1-op-*dichlorobenzylideneindene*, yellow crystals, m. p.

98·5—99·5°, and 3-op-*dichloro-α-hydroxybenzyl*-1-op-*dichloro-benzylideneindene,* $C_6H_4\!\!<^{C(:CH\cdot C_6H_3Cl_2)^{-}}_{C(CH[OH]\cdot C_6H_3Cl_2)}\!\!\gg CH$, yellow crystals, m. p. 204—205°; the former of these, which is the more soluble in methyl alcohol, yields 3-op-*dichlorobenzylindene,* colourless crystals, m. p. 99—101°, by reduction. 3-*op-dichloro*-benzylindene and *p*-chlorobenzaldehyde yield 3-op-*dichloro-benzyl*-1-p-*chlorobenzylideneindene,* $C_6H_4\!\!<^{C(:CH\cdot C_6H_4Cl)^{-}}_{C(CH_2\cdot C_6H_3Cl_2)}\!\!\gg CH$, yellow crystals, m. p. 114—115° (in this and in other condensations in which a mono-substituted indene reacts with the second aldehyde, the boiling with the methyl-alcoholic potassium hydroxide is not prolonged beyond a few minutes), which is converted by the further action of boiling methyl-alcoholic potassium hydroxide into 3-p-*chlorobenzyl-1-op-dichlorobenzylideneindene,*

$$C_6H_4\!\!<^{-C(CH_2\cdot C_6H_4Cl)}_{C(:CH\cdot C_6H_3Cl_2)}\!\!\gg CH,$$
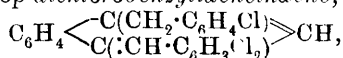
yellow crystals, m. p. 175—177°; the last substance is obtained directly from 3-*p*-chlorobenzylindene and *op*-dichlorobenzaldehyde, and is unaffected by boiling methyl-alcoholic potassium hydroxide.

3-*op*-Dichlorobenzylindene and benzaldehyde yield 3-op-*dichlorobenzyl*-1-*benzylideneindene,* yellow crystals, m. p. 73—74°. 3-Benzylindene and *op*-dichlorobenzaldehyde yield 3-*benzyl*-1-op-*dichlorobenzylideneindene,* yellow crystals, m. p. 117—118°. Each of this pair of isomeric benzfulvenes is quite unaffected by boiling methyl-alcoholic potassium hydroxide, 5% sodium methoxide solution, or concentrated ammonia solution.

Indene and *p*-tolualdehyde yield 1-p-*tolylideneindene,* yellow crystals, m. p. 91—92°, which is reduced to 3-p-*methylbenzylindene,* almost colourless crystals, m. p. 27—29°, b. p. 218—222°/ 12 mm., by aluminium amalgam. 3-*p*-Methylbenzylindene and benzaldehyde yield 3-p-*methylbenzyl-1-benzylideneindene,* yellow crystals, m. p. 106—107°. 3-Benzylindene and *p*-tolualdehyde yield 3-*benzyl*-1-p-*tolylideneindene,* yellow crystals, m. p. 98—100°. Each of this pair of isomerides gave by boiling with methyl-alcoholic potassium hydroxide a substance, m. p. about 70°, which is doubtless a mixture of the two isomerides.

Indene and *p-iso*propylbenzaldehyde gave 1-p-iso*propylbenzyl-ideneindene,* orange-yellow crystals, m. p. 60—61°, which yields 3-p-iso*propylbenzylindene,* almost colourless crystals, m. p. 32°. 3-*p-iso*Propylbenzylindene and benzaldehyde yield 3-p-iso*propyl-benzyl-1-benzylideneindene,* yellow needles, m. p. 105—107°. 3-Benzylindene and *p-iso*propylbenzaldehyde yield 3-*benzyl*-1-p-iso*propylbenzylideneindene,* yellow needles, m. p. 93—94°, which is converted into a mixture, m. p. 71—73°, of the two isomerides by prolonged boiling (ten hours) with methyl-alcoholic potassium hydroxide.

3-*p*-Chlorobenzylindene and benzaldehyde yield 3-p-*chlorobenzyl-1-benzylideneindene,* yellow needles, m. p. 98—99°, and 3-benzyl-

indene and .*p*-chlorobenzaldehyde yield 3-*benzyl*-1-p-*chlorobenzyl-ideneindene*, yellow needles, m. p. 88—89°. The last compound is converted by boiling for eight hours with methyl-alcoholic potassium hydroxide partly into a mixture, m. p. 79—81°, of the two isomerides and partly into 3-*benzyl*-1-p-*chlorobenzylindene*, colourless needles, m. p. 183—184°, which is also produced by reducing the benzfulvene with aluminium amalgam and moist ether.

3-*p*-Methylbenzylindene and *p*-chlorobenzaldehyde yield 3-p-*methylbenzyl*-1-p-*chlorobenzylideneindene*, large yellow crystals, m. p. 95—96°, together with a small quantity of a *substance*, colourless needles, m. p. 181—183°, which is probably 1-p-*chlorobenzyl* - 3 - p -*methylbenzylindene*. 3 - *p* - Chlorobenzylindene and *p*-tolualdehyde yield a mixture of a colourless substance, m. p. 182—184° (which is shown to be 1-*p*-chlorobenzyl-3-*p*-methylbenzyl-indene), and a small quantity of a yellow substance, m. p. 91—92°, which appears to be 3-*p*-methylbenzyl-1-*p*-chlorobenzylideneindene in a not quite pure state.   C. S.

Isomerism of Benzfulvenes and Indenes. H.-M. WÜEST (*Annalen*, 1918, **415**, 291—337. Compare two preceding abstracts).—With regard to the eight pairs of isomerides described by Thiele and Merck and by Bernthsen (*loc. cit.*), no generalisation in respect of the stability of one of the two isomerides can be drawn, partly because no conclusions can be made from the nature of the groups introduced and partly because the transformation from the one isomeride into the other indubitably occurs only in two cases and fails entirely only in two other cases. A new series of benzfulvenes has therefore been examined.

The simplest case of isomerism is represented by a 3-substituted benzfulvene (formula I) and the isomeric ω-substituted 3-methyl-benzfulvene (formula II).

$$CH_2R$$ $$CHR$$

(I.)   (II.)
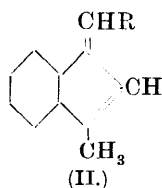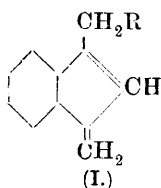
3-*Methylbenzfulvene*, $C_6H_4{<}_{C(:CH_2)}^{---CMe}{>}CH$,   an unstable, faintly yellow, intensely odorous oil, b. p. 102—104°/11 mm. (*picrate*, yellow needles, m. p. 125·5—126·5°), is readily obtained by boiling a mixture of 3-methylindene, paraform-aldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for twelve minutes, but in no other case could a 3-sub-stituted benzfulvene of type I be obtained, the product being always the ω-substituted 3-methylbenzfulvene of type II, owing to the isomerising action of the alkali used as condensing agent.

Thus 3-benzylindene and paraformaldehyde yield 1-benzylidene-3-methylindene (*picrate*, pale red needles, m. p. 90—91°), 3-*p*-methoxybenzylindene and formaldehyde yield a mixture of 1-*p*-anisylidene-3-methylindene and 1-*p-anisylidene-3-ethylindene*, $C_{19}H_{18}O$, yellow needles, m. p. 100·5—101·5° (neither of these is changed by boiling for eight hours with methyl-alcoholic potassium hydroxide), 3-methylindene and furfuraldehyde yield, after condensation with methyl-alcoholic potassium hydroxide for forty-two hours at the ordinary temperature, 1-*furfurylidene-3-methylindene*, deep yellow needles, m. p. 77—77·5° (this compound, which forms a *picrate*, dark red needles, m. p. 97—98°, is also obtained by boiling 3-furylmethylindene, paraformaldehyde, absolute alcohol, and methyl-alcoholic potassium hydroxide for a few seconds and cooling rapidly), and 3-methylindene and benzophenone yield *ωω-diphenyl-3-methylbenzfulvene*, yellow crystals, m. p. 120—121° (*picrate*, pale red needles, m. p. 149—151°), the last condensation being effected by boiling with alcoholic potassium ethoxide for seventeen hours. The last-mentioned benzfulvene is also obtained by boiling a mixture of 3-benzhydrylindene, paraformaldehyde, absolute alcohol, and 28% methyl-alcoholic potassium hydroxide for one hour.

The preceding four benzfulvenes of type II are all intensely yellow, and are reducible by aluminium amalgam and moist ether; the reduction of ωω-diphenyl-3-methylbenzfulvene proceeds very slowly and incompletely, the product being 3-*benzhydryl-1-methyl-indene*, $C_6H_4{<}^{C(CHPh_2)}_{CHMe}{>}CH$, colourless needles, m. p. 162·5—163·5°.

The groups phenyl, *p*-anisyl, benzhydryl, and furyl in all possible pairs have been systematically introduced into the ω- and the 3-positions in benzfulvene. The case of the pair phenyl and *p*-anisyl has been investigated by Thiele and Merck (*loc. cit.*); both isomerides are known, 3-benzyl-1-*p*-anisylideneindene being the more stable. Other pairs of isomerides which exhibit transformation are the following: 3-Benzhydrylindene and benzaldehyde are condensed by methyl-alcoholic potassium hydroxide, after one day at the ordinary temperature, or after thirty seconds in the boiling solution, yielding 3-*benzhydryl-1-benzylideneindene*, pale yellow needles, m. p. 131·5—132·5°. If the boiling is prolonged to five minutes, a difficultly separable mixture of this and its isomeride, *ωω-diphenyl-3-benzylbenzfulvene*, deep yellow, quadratic leaflets, m. p. 130—130·5°, is obtained. The transformation is easily and completely effected by boiling a mixture of 3-benzhydrylindene, benzaldehyde, pyridine, and 28% methyl-alcoholic potassium hydroxide for one minute. This method of preparing ωω-diphenyl-3-benzylbenzfulvene is much to be preferred to that in which 3-benzylindene and benzophenone are condensed by methyl-alcoholic potassium hydroxide, since in the latter considerable quantities of benzhydrol are formed. Thiele and Merck (*loc. cit.*) prepared 3-benzhydryl-1-*p*-anisylideneindene at the ordinary

temperature. It is also obtained at the b. p. after thirty seconds, but after boiling with alkali for one hour in alcoholic or pyridine solution, is transformed into ωω-*diphenyl*-3-p-*methoxybenzylbenzfulvene*, yellow needles, m. p. 127—128°. The preparation of the two following pairs of isomerides containing furyl and phenyl or *p*-anisyl groups at first presented great difficulty, on account of the extreme ease with which the unstable isomeride is converted into the stable one. 1-*Furfurylideneindene* (ω-*furylbenzfulvene*),

$$C_6H_4 <^{\overline{\qquad\qquad}CH}_{C(:CH \cdot C_4H_3O)} > CH,$$ yellow needles, m. p. 86—86·5°

(*picrate*, red needles, m. p. 103—105°), prepared from indene and furfuraldehyde in boiling methyl-alcoholic potassium hydroxide (five minutes), is reduced by aluminium amalgam and moist ether

to 3-*furylmethylindene*, $$C_6H_4 <^{\overline{\qquad\qquad}CH_2}_{C(CH_2 \cdot C_4H_3O)} > CH,$$ almost colour-

less liquid with a pleasant, aromatic odour, b. p. 166—168°/15 mm. From the last compound and benzaldehyde 3-*furylmethyl*-1-*benzylideneindene*, yellow needles, m. p. 93—94·5° (clear at 98°), must be obtained merely by shaking with hot methyl-alcoholic potassium hydroxide and immediately pouring the mixture into water. If the mixture is boiled even for only thirty seconds, the substance is transformed into 1-*furfurylidene*-3-*benzylideneindane*,

$$C_6H_4 <^{C(:CH \cdot C_4H_3O)}_{C(==CHPh)} > CH_2,$$
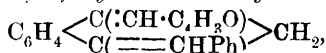
faintly yellow needles, m. p. 160·5—161°, which by boiling with methyl-alcoholic potassium hydroxide for four hours is converted into 1-*furfurylidene*-3-*benzylindene*, yellow needles, m. p. 126—127°; the last substance is obtained directly by the condensation of 3-benzylindene and furfuraldehyde. Using *p*-anisaldehyde in place of benzaldehyde, the following substances are obtained by methods similar to the preceding: 1-*anisylidene*-3-*furylmethylindene*, yellow leaflets, m. p. 88—89°, 1-*anisylidene*-3-*furfurylideneindane*, yellow needles, m. p. 150—150·5°, and 3-p-*methoxybenzyl*-1-*furfurylideneindene*, golden-yellow leaflets, m. p. 127—128°. The condensation of 3-benzhydrylindene and furfuraldehyde by methyl-alcoholic potassium hydroxide, whether boiled for three seconds or for one hour, yields 3-*benzhydryl*-1-*furfurylideneindene*, yellow needles, m. p. 170—170·5°, which is not changed by alkali even in the presence of pyridine. The isomeride was not prepared.

An examination of all the preceding pairs of isomerides shows that in every transformation the double linking shifts, so that the partial valencies are balanced as much as possible, and consequently the more saturated system is formed. In the four cases in which the substituents are a methyl group and an aromatic group, the more saturated system is formed so easily that the more unsaturated isomeride is unknown. When the substituents are two aromatic groups, a partial balance of the valencies occurs in both isomerides, and the transformation is rendered more difficult and leads to the formation of the isomeride in which the exocyclic

double linking is conjugated with the more strongly unsaturated substituent; this isomeride is therefore the more intensely coloured of the pair.

1-*Furfurylidene*-3-*furylhydroxymethylindene*,

$$C_6H_4 \begin{matrix} C(CH[OH] \cdot C_4H_3O) \\ C(:CH \cdot C_4H_3O) \end{matrix} \!\!\!\! \begin{matrix} \\ \end{matrix} \!\!\!\! > CH,$$
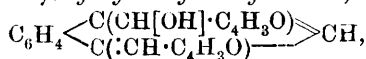
yellow needles, m. p. 114·5—115°, obtained by condensing indene and furfuraldehyde by means of cold methyl-alcoholic potassium hydroxide for six hours, is reduced by aluminium amalgam and moist ether to 1 : 3-*difurfurylideneindane*,

$$C_6H_4 \begin{matrix} C(:CH \cdot C_4H_3O) \\ C(:CH \cdot C_4H_3O) \end{matrix} \!\!\!\! > CH_2,$$
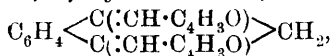
faintly yellow needles, m. p. 132·5—133·5°, which is also obtained by boiling for one minute with alcoholic alkali 3-*furylmethyl*-1-*furfurylideneindene*, yellowish-brown needles, m. p. 103—104°, prepared from 3-furylmethylindene and furfuraldehyde.

3-Arylated benzfulvenes containing two aliphatic groups in the ω-positions are quite generally incapable of transformation. ω-*Methyl*-ω-*ethylbenzfulvene*, prepared by boiling indene and methyl ethyl ketone with alcoholic alkali for five hours, is a faintly yellow oil, b. p. 151—152°/15 mm. (*picrate*, orange needles, m. p. 87·5—88°, sintering at 85°), which is reduced by sodium and absolute alcohol to 3-iso*butylindene*, a colourless oil, b. p. 116—118°/12 mm. The last substance and benzophenone condense when boiled for twenty-three hours with pyridine and alcoholic alkali to form ωω-*diphenyl*-3-iso*butylbenzfulvene*, yellow needles or stout prisms, m. p. 91—92°. 3-*Benzhydryl*-ω-*methyl*-ω-*ethylbenzfulvene*, prepared from 3-benzhydrylindene and methyl ethyl ketone and boiling alcoholic alkali (fifteen minutes), is a faintly yellow, crystalline powder, m. p. 149·5—151°. 3-iso*Propylindene* and benzophenone yield ωω-*diphenyl*-3-iso*propylbenzfulvene*, yellow, crystalline powder, m. p. 127—128°. 3-Benzhydrylindene and acetone yield 3-*benzhydryl*-ωω-*dimethylbenzfulvene*, yellow, crystalline powder, m. p. 174—175°.

The reduction of 3-benzhydryl-1-benzylideneindene and of ωω-diphenyl-3-benzylbenzfulvene by aluminium amalgam and moist ether leads to the same product, namely, a mixture of a *substance*, $C_{29}H_{24}$, hard crystals, m. p. 130—131°, and an isomeric *substance*, slender needles, m. p. 137—138°, which are the two benzylbenzhydrylindenes; also the reduction of ωω-diphenyl-3-iso*butylbenzfulvene* yields a mixture of two isomerides, namely, *benzhydryl*iso*butylindene* I, colourless needles, m. p. 121—123°, and *benzhydryl*iso*butylindene* II, slender needles, m. p. 94—95·5°. The latter is obtained from the former by boiling with alcoholic alkali for thirty minutes, and also from 3-benzhydryl-ω-methyl-ω-ethylbenzfulvene by reduction with sodium and alcohol.

The reduction of benzfulvenes in ethereal solution with platinum-black and hydrogen leads to the formation of indanes. Thus 3-benzhydryl-ωω-dimethylbenzfulvene yields 3-*benzhydryl*-1-iso*propylindane*, slender needles, m. p. 126·5—127·5°, and ωω-di-

phenyl-3-*iso*butylbenzfulvene yields 1-*benzhydryl-3-isobutylindane,*
colourless crystals, m. p. 104—106°.   C. S.

Action of Sulphur on Organic Compounds. I. Hydrocarbons. LUDWIK SZPERL (*Chemik Polski,* 1917, **15,** 10—18; from *Chem. Zentr.,* 1918, i, 908. Compare following abstracts).—A review of the literature of the subject.   H. W.

Action of Sulphur on Organic Compounds. II. Diphenylmethane and Fluorene. Dibenzyl. LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski,* 1917, **15,** 19—22; from *Chem. Zentr.,* 1918, i, 908—909. Compare preceding abstract).—Contrary to the statement of Kaufmann, the authors find that diphenyldiphenylene-ethylene, $CPh_2{:}C{<}{}^{C_6H_4}_{C_6H_4}$, is the main product formed when a mixture of diphenylmethane and fluorene is heated with sulphur until hydrogen sulphide ceases to be evolved; the substance separates from acetone in needles containing acetone of crystallisation, which is lost on exposure to air. It then has m. p. 229—229·5°. Tetraphenylethane, tetraphenylethylene, tetraphenylene-ethane, and tetraphenylene-ethylene are simultaneously produced.

Tetraphenylthiophen, $C_{28}H_{20}S$, m. p. 183—184°, is the sole product of the action of sulphur on dibenzyl at 260°.   H. W.

Action of Sulphur on Organic Compounds. III. Benzyl Alcohol, Diphenylcarbinol. LUDWIK SZPERL and. TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski,* 1917, **15,** 23—27; from *Chem. Zentr.,* 1918, i, 909. Compare preceding abstracts).—Visible reaction between benzyl alcohol and sulphur commences at about 180°, water, hydrogen sulphide, and benzaldehyde being evolved. The product of the reaction contains, in addition, benzoic acid, tetraphenylthiophen, stilbene, and small quantities of needles, m. p. 127—130°. The main products are tetraphenylthiophen and benzoic acid.

Diphenylcarbinyl ether, $C_{26}H_{22}O$, m. p. 108·5—109°, together with small quantities of benzophenone and possibly traces of diphenylmethane, is produced when diphenylcarbinol is heated with sulphur at 180°, and the action is stopped when water vapour ceases to be evolved. The formation of the ether is attributed to the catalytic action of sulphur on the alcohol. Similarly, benzyl alcohol when heated with 0·1 gram-atom of sulphur gives a 20% yield of dibenzyl ether, b. p. 295—298°. It is therefore to be assumed that the products isolated from the alcohols are due to the action of sulphur on the ethers, and not on the alcohols themselves.   H. W.

Action of Sulphur on Organic Compounds. IV. Dibenzyl Ether and Benzhydryl Ether. LUDWIK SZPERL and TADEUSZ WIERUSZ-KOWALSKI (*Chemik Polski,* 1917, **15,** 28—33; from *Chem. Zentr.,* 1918, i, 909—910. Compare preceding abstracts).—With the object of verifying the hypothesis that the formation of the corresponding ethers from benzyl alcohol and diphenylcarbinol

is to be attributed to the catalytic action of sulphur, and that other possible admixtures are without influence, the following experiments have been performed. Pure benzyl alcohol was heated at 180° for several hours alone and with intermittent treatment with hydrogen sulphide; the results were negative. Slightly impure diphenylcarbinol (prepared from benzaldehyde and phenyl magnesium bromide and containing traces of magnesium, chlorine, etc.) gave after three hours at 150—152° an almost quantitative yield of benzhydryl ether, but the change proceeded less rapidly with a purer material.

Benzyl ether, when heated with sulphur below 200°, yielded hydrogen sulphide, benzaldehyde, benzoic acid, stilbene, and tetraphenylthiophen. Diphenylcarbinyl ether gave benzophenone and tetraphenylethylene. The reactions occurred, therefore, in precisely the same manner as with the corresponding alcohols; they may be represented by the schemes: $2(PhCH_2)_2O + 2S = 2H_2S + 2C_6H_5 \cdot CHO + CHPh:CHPh$, $2(Ph_2CH)_2O + 2S = 2H_2S + 2COPh_2 + CPh_2:CPh_2$. H. W.

Attempted Synthesis of 3 : 4 : 8 : 9-Dibenzopyrene. RICHARD WEITZENBÖCK (*Monatsh.*, 1918, **39**, 307—313).—By the synthetic method already discovered for pyrene (Weitzenböck, A., 1913, i, 259), it should be possible to produce pyrene derivatives containing condensed hydrocarbon nuclei; the paper records an unfinished investigation in this direction.

1 : 1'-Dimethyl-2 : 2'-dinaphthyl, prepared by the action of copper on 2-iodo-1-methylnaphthalene (Scholl, this vol., i, 484), is accompanied by a *substance*, $C_{22}H_{16}$, leaflets, m. p. 314—316°; *picrate*, brick-red needles, m. p. 199—201°. When brominated in boiling nitrobenzene solution, 1 : 1'-dimethyl-2 : 2'-dinaphthyl is converted into 1 : 1'-*dibromomethyl*-2 : 2'-*dinaphthyl*, $C_{22}H_{16}Br_2$, needles, m. p. 200—201°, which reacts with aqueous-alcoholic potassium cyanide, yielding 2 : 2'-*dinaphthylene*-1 : 1'-*diacetonitrile*, crystals, m. p. 264°; this on hydrolysis with alcoholic potassium hydroxide at 150° gives 2 : 2'-*dinaphthylene*-1 : 1'-*diacetic acid*,

$$C_6H_4 {<}^{CH=\!=\!=CH}_{C(CH_2 \cdot CO_2H)} {>} C\!-\!C {<}^{CH=\!=\!=CH}_{C(CH_2 \cdot CO_2H)} {>} C_6H_4,$$
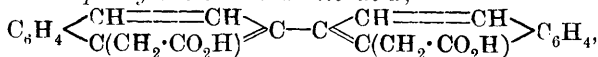
From this, by the stages represented by formulæ I and II, it should be possible to obtain 3 : 4 : 8 : 9-dibenzopyrene (formula III)

(I.)   (II.)   (III.)
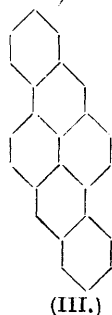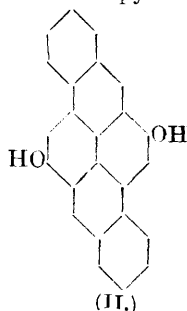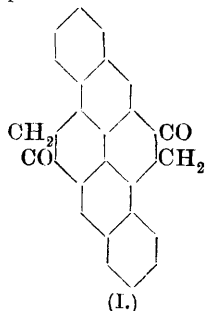
· In a preliminary investigation with a view to a new pyrene synthesis, *o*-iodophenyldichloropropionic acid, obtained by the action of chlorine on a carbon disulphide solution of *o*-iodocinnamic acid, was steam distilled in the presence of excess of sodium carbonate, with formation of o-*iodostyryl chloride*, $C_6H_4I \cdot CH:CHCl$, b. p. 151°/24 mm.   D. F. T.

Synthesis of the Isomeric Hydrocarbons 1 : 2 : 5 : 6-Dibenzanthracene and 3 : 4 : 5 : 6 - Dibenzphenanthrene. RICHARD WEITZENBÖCK and ALBERT KLINGLER (*Monatsh.*, 1918, **39**, 315—323. Compare Weitzenböck and Lieb, A., 1912, i, 547). —When heated with *o*-nitrobenzaldehyde in acetic anhydride solution, potassium phenylenediacetate undergoes conversion into o-*nitrobenzylidene*-p-*phenylenediacetic acid*,

$$CO_2H \cdot CH_2 \cdot C_6H_4 \cdot C(CO_2H):CH \cdot C_6H_4 \cdot NO_2,$$
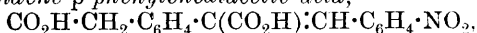
colourless needles, m. p. 236°, which by further treatment can be made to yield *di*-o-*nitrobenzylidene*-p-*phenylenediacetic acid*, $NO_2 \cdot C_6H_4 \cdot CH:C(CO_2H) \cdot C_6H_4 \cdot C(CO_2H):CH \cdot C_6H_4 \cdot NO_2$, pale yellow prisms, m. p. 308° (decomp.). This substance on reduction in ammoniacal solution with ferrous hydroxide gives *di*-o-*aminobenzylidene*-p-*phenylenediacetic acid*,

$$NH_2 \cdot C_6H_4 \cdot CH:C(CO_2H) \cdot C_6H_4 \cdot C(CO_2H):CH \cdot C_6H_4 \cdot NH_2,$$
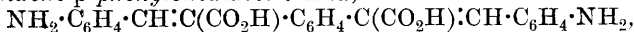
yellow needles, m. p. near 276°, which by diazotisation and subsequent treatment with copper powder can be made to yield a mixture of 1 : 2 : 5 : 6-dibenzanthracenedicarboxylic acid and 3 : 4 : 5 : 6-dibenzphenanthrenedicarboxylic acid; these were not separated, the mixture being directly converted by heating under reduced pressure into a mixture of the corresponding hydrocarbons, which were then separated by crystallisation from acetic acid. The less soluble 1 : 2 : 5 : 6-*dibenzanthracene* (formula I) forms silvery leaflets, m. p. 262° (*picrate*, $C_{22}H_{14},2C_6H_3O_7N_3$, orange needles, m. p. 214°), gives a red solution with alkaline sodium hyposulphite solution, and is oxidisable by potassium dichromate in acetic acid to 1 : 2 : 5 : 6-*dibenzanthraquinone*, $C_{22}H_{12}O_2$, orange needles, m. p. 248—249°, whilst the more soluble 3 : 4 : 5 : 6-*dibenzphenanthrene* (formula II) forms colourless needles, m. p. 145—146°.
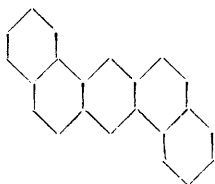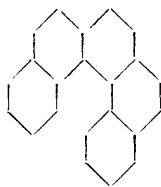
(I.)   (II.)

                                    D. F. T.

Preparation of Hydrogenated Compounds. FARBENFABRIKEN VORM FRIEDR. BAYER & Co. (D.R.-P., 305347; from *Chem. Zentr.*, 1918. i, 977).—The process depends on the action of alkali or alkali earth metals and alcohols on isocyclic or heterocyclic bases

in the presence of an inert solvent; the alcohol is preferably added at the same rate as it is used in the reaction. Thus tetrahydro-α-naphthylamine is formed when a solution of α-naphthylamine in alcohol is added to a mixture of solvent naphtha and sodium at a temperature above 130°; with a solvent of lower b. p., such as toluene, dihydro-α-naphthylamine is obtained. 2-Methylquinoline, when hydrogenated at above 130°, yields tetrahydro-2-methylquinoline, which gives a characteristic blood-red coloration with ferric chloride and potassium ferricyanide. The picrate has m. p. 153—154°.   H. W.

Phenylpropionamidine. ROLAND SCHOLL [with E. BERTSCH] (*Monatsh.*, 1918, **39**, 238—240).—Phenylpropionamidine,

$$NH{:}CEt{\cdot}NHPh,$$

m. p. 72—73° (Michael and Wing, A., 1886, 148, give 68°), is formed when propionitrile is heated with aniline hydrochloride in a sealed tube at 170—180° for twelve hours; *hydrochloride*, hygroscopic; *hydrogen oxalate*, m. p. 141—142°; *picrate*, m. p. 152—153°.   D. F. T.

Phenyl and Alkyl Phenyl Esters of Phosphorous Acid. T. MILOBENDZKI and K. SZULGIN (*Chemik Polski*, 1917, **15**, 66—75; from *Chem. Zentr.*, 1918, i, 914—915. Compare this vol., i, 477, 478, 479).—The action of alcohols on triphenyl phosphite leads to replacement of the phenyl groups, but isomerisation occurs simultaneously with the formation of phosphinic esters: $P(OPh)_3 + 3PrOH = PPrO(OPr)_2 + 3PhOH$. Diphenyl esters may be obtained by the use of sodium alkyloxides:

$$P(OPh)_3 + PrONa = OPr{\cdot}P(OPh)_2 +$$
$$PhONa \xrightarrow{HCl\ gas} OH{\cdot}P(OPh)_2 + C_3H_7Cl.$$
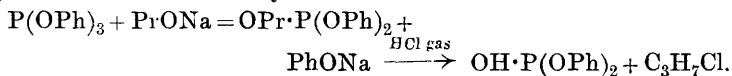
Triphenyl phosphite, b. p. 235°/18 mm., is obtained in 91% yield by the gradual addition of phosphorus trichloride to a mixture of phenol and pyridine. It does not react with cold alcohols. Methyl alcohol at 225° transforms it completely into dimethyl methylphosphinate, b. p. 181°/754 mm. *Dipropyl propylphosphinate* (formed, together with small quantities of tripropyl phosphite, in a similar manner) is a colourless liquid, b. p. 126°/18 mm., D_0^{22} 1·0327, D_4^{22} 1·0324. *Tripropyl phosphite* (by action of sodium propoxide [4 parts] and triphenyl phosphite [1 part] in benzene solution) has b. p. 103°/24 mm., whilst *tributyl phosphite* has b. p. 120°/10 mm. The action of sodium propoxide (1 part) on triphenyl phosphite (1 part) leads to the formation of *propyl diphenyl phosphite*, b. p. 203—204°/24 mm., D_0^{19} 1·1153, D_4^{19} 1·1149. *Butyl diphenyl phosphite* has b. p. 198°/12 mm., D_0^{22} 1·0918, D_4^{22} 1·0917. Propyl diphenyl phosphite is obtained in better yield by the gradual addition of diphenylphosphorous chloride, $P(OPh)_2Cl$, to a mixture of propyl alcohol and pyridine; it is slowly hydrolysed by water or alkalis.

Diphenyl phosphite, b. p. 218—219°/25 mm., is prepared by

saturating ice-cold diphenyl propyl phosphite with hydrogen chloride (1 mol.). The alkaline solution of the substance gives with ferric chloride a *precipitate* of the composition (PhO)(FeO)POH [?].   H. W.

o-**Nitrosophenol. III. Preparation of** *o*-**Nitrosophenol as a Lecture Experiment [Reagent for Copper].** Oskar Baudisch (*Ber.*, 1918, **51**, 1058—1059. Compare A., 1916, i, 33).—A solution containing *o*-nitrosophenol may be quickly prepared as follows: a crystal or two of *o*-nitrophenol is dissolved in a few drops of hot acetic acid, cooled, diluted a little, covered with light petroleum, and shaken with a trace of zinc dust. The aqueous layer becomes pink owing to the formation of the zinc salt of *o*-nitrosophenol, but the free reagent is chiefly contained in the supernatant, green layer. If this solution is shaken with a trace of a copper salt, the petroleum becomes colourless and the aqueous layer deep red. This test for copper is said to be more sensitive than the ferrocyanide reaction.   J. C. W.

Preparation of Picramic Acid. Grete Egerer (*J. Biol. Chem.*, 1918, **35**, 565—566).—Finely powdered picric acid (20 grams) is dissolved in 300 c.c. of alcohol, and 125 c.c. of ammonia (0·880) are added. After cooling to 30°, hydrogen sulphide is passed in rapidly, so that the temperature rises to 50—55° in fifteen minutes. The flask is then cooled in ice, while the stream of hydrogen sulphide is maintained for forty-five minutes. Crystals of ammonium picramate are deposited, and are collected and decomposed by the addition of 60 c.c. of acetic acid (1 part of glacial acid to 4 parts of water). After vigorous stirring, the picramic acid is collected, washed with a little water, and recrystallised from boiling water. Yield, 75 to 80% of the theoretical.   H. W. B.

Preparation of Derivatives of *p*-**Aminophenol.** Society of Chemical Industry in Basle (Brit. Pat. 116920, 1917; A., 1901, i, 533).—*p*-Aminophenyl allyl ether (Spiegel & Sabbath) is poisonous, but its acyl derivatives are not poisonous in therapeutic doses, and possess narcotic, sedative, and anti-neuralgic properties. *p*-Acetylaminophenyl allyl ether forms lustrous leaflets, m. p. 94°, readily soluble in alcohol, ether, and acetone, and somewhat readily so in hot water. The *lactyl* derivative forms lustrous leaflets, m. p. 87°, readily soluble in alcohol, ether, and benzene, and somewhat readily so in hot water; the iso*valeryl* derivative forms small, lustrous needles, m. p. 95°, and the α-*bromo*iso*valeryl* derivative lustrous leaflets, m. p. 131°.   A. S.

Compounds of *p*-**Phenetidine.** L. Reutter (*Schweiz. Apoth.-Zeit.*, 1917, **55**, 692; from *Chem. Zentr.*, 1918, i, 825—826).—Di-*p*-phenetylthiocarbamide, lead carbonate, alcohol, and aqueous potassium cyanate reacting first in the cold and then at 45° yield the *nitrile*, OEt·C$_6$H$_4$·NH·C(CN):N·C$_6$H$_4$·OEt, yellow crystals,

m. p. 104°, which is converted into a *substance*, $C_{18}H_{21}O_2N_3S$, yellow prisms, m. p. 124°, by shaking with yellow ammonium sulphide for three days, and finally warming at 30—35°, and into a *substance*, $C_{18}H_{22}O_3N_3Cl$, whitish-yellow crystals, m. p. 220°, by dissolution in concentrated hydrochloric acid on the water-bath.

C. S.

Preparation of Guaiacol. ERNST H. ZOLLINGER and HERMANN RÖHLING (D.R.-P., 305281; from *Chem. Zentr.*, 1918, i, 977).—A weak base such as sodium carbonate or sodium hydrogen carbonate is gradually added to a mixture of catechol with the alkali or alkali earth salts of methylsulphuric acid in the presence of veratrole as diluent at 160—180°; the yield is more than 85% of that theoretically possible. H. W.

Polyhydric Mercaptans of the Benzene Series. VI. Homologous Dithiolbenzenes. J. POLLAK and B. SCHADLER (*Monatsh.*, 1918, **39**, 129—148. Compare Pollak and others, A., 1915, i, 529; 1914, i, 39; 1910, i, 734; 1909, i, 791).—By treatment with fuming sulphuric acid, *m*-xylene was converted into a mixture of disulphonic acids, from which by the action of phosphorus pentachloride a mixture of the corresponding *m*-xylene-2:4-disulphonyl chloride and *m*-xylene-2:5-disulphonyl chloride was obtained (compare Pfannenstill, A., 1892, 1340). The crystalline 2:4-disulphonyl chloride on reduction with tin and hydrochloric acid gives 2:4-*dithiol*-m-*xylene*, $C_6H_2Me_2(SH)_2$, leaflets, m. p. 123—125° (*acetyl* derivative, $C_6H_2Me_2(SAc)_2$, leaflets, m. p. 76·5—79°), which reacts with chloroacetic acid and ethyl chloroformate respectively in alkaline solution, yielding m-*xylene-2:4-dithiolacetic acid*, $C_6H_2Me_2(S\cdot CH_2\cdot CO_2H)_2$, colourless, stellar aggregates, m. p. 185—189°, and 2:4-*diethylthiocarbonato*-m-*xylene*,

$$C_6H_2Me_2(S\cdot CO_2Et)_2,$$
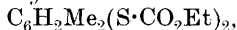
long needles, m. p. 61—63°, and is converted by aqueous hydrogen peroxide into a *substance*, $(C_6H_2Me_2S_2)_n$, needles, m. p. 252—255°; with picryl chloride, the mercaptan reacts, producing 2:4-*dipicrylthiol*-m-*xylene*, $C_6H_2Me_2[S\cdot C_6H_2(NO_2)_3]_2$, orange-coloured needles with $1C_6H_6$, m. p. 258—259·5°. Treatment with methyl sulphate in the presence of alkali converts the mercaptan into 2:4-*dimethylthiol*-m-*xylene*, $C_6H_2Me_2(SMe)_2$, needles, m. p. 83—84·5°, which reacts with chlorine, yielding a *substance*, $C_{10}H_{11}S_2Cl_3$, and with bromine in chloroform solution, giving an *additive* compound, $C_6H_2Me_2(SMe)_2Br_2$, deep red needles, decomp. 99—102°; this regenerates the parent dimethylthiolxylene when shaken in chloroform solution with aqueous sodium hydrogen sulphite. Oxidation with aqueous potassium permanganate converts the dimethylthiolxylene into the *disulphone*, $C_6H_2Me_2(SO_2Me)_2$, needles, m. p. 187—188°.

In a similar manner, the isomeric, oily *m*-xylene-2:5-disulphonyl chloride can be reduced to an oily 2:5-*dithiol*-m-*xylene*, b. p. 142—144°/9 mm., which reacts with chloroacetic acid in alkaline

solution, giving m-*xylene*-2 : 5-*dithiolacetic acid*, stellar aggregates, m. p. 158—161°, and with picryl chloride forming 2 : 5-*dipicryl-thiol*-m-*xylene*, crystals, m. p. 211—213°. The 2 : 5-*dimethylthiol-m-xylene*, b. p. 167—169°/14 mm., obtained by methylation with methyl sulphate, undergoes substitution when treated in chloroform solution with bromine, yielding a *bromo*-derivative,

$$C_6HBrMe_2(SMe)_2,$$
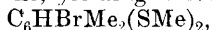
crystalline scales, m. p. 122—123°. The unexpected greater ease of bromination of this dimethylthiolxylene as compared with its 2 : 4-isomeride led to a doubt as to whether the relative structures of these substances are really as assumed above (compare Zincke and Krüger, A., 1913, i, 44), but an attempt to decide this matter by heating the 2 : 4-disulphonyl chloride with thionyl chloride in the hope of replacing the –SO_2Cl groups by chlorine atoms was unsuccessful, the product being a *substance*, $C_8H_2O_2Cl_4$, crystalline scales, m. p. 76—77°, possibly 2 : 4-dichloro-m-phthaloyl chloride. A somewhat similar reaction to this was observed between 1 : 3-dimethoxybenzene-4 : 6-disulphonyl chloride and thionyl chloride at 170°, the product being a substance, $C_8H_6O_2Cl_4$, needles, m. p. 95—98°, possibly of the structure $C_6H_2Cl_2(O\cdot CH_2Cl)_2$ (compare Meyer, A., 1916, i, 134).

2 : 6(?)-*Dithiol*-p-*xylene*, b. p. 145·5°/11·5 mm. (*diacetyl* derivative, needles, m. p. 79·5—82·5°; p-*xylene*-2 : 6-*dithiolacetic acid* derivative, needles, m. p. 170·5—174·5°; *dipicryl* derivative, yellow, crystalline solid, m. p. 251—255°; *dimethyl* derivative, needles, m. p. 92—94°), is obtainable from p-xylene through the disulphonyl chloride.   D. F. T.

Polyhydric Mercaptans of the Benzene Series. VII. Substituted Thiolbenzenes. J. POLLAK, LUZIE VON FIEDLER, and HEINRICH ROTH (*Monatsh.*, 1918, **39**, 179—200. Compare Pollak and Schadler, preceding abstract).—The effect of the introduction of a methyl group on the m. p. of the polyhydric mercaptans is rather irregular; thus 1 : 3-dithiolbenzene and 2 : 4-dithiol-m-xylene have m. p. 25° and 121° respectively (*loc. cit.*), whereas the substitution of a methyl group into the nucleus of trithiolbenzene causes a small depression of the m. p. Further compounds were therefore prepared with the view of investigating the influence of such substitution more widely, but no general regularities were observed either with the m.p.'s or b.p.'s.

1-*Ethylbenzene*-2 : 4-*disulphonic acid* (*barium* salt, crystalline with $2\frac{1}{2}H_2O$), obtained by the action of fuming sulphuric acid on benzene, was converted into the corresponding acid *chloride*, $C_6H_3Et(SO_2Cl)_2$, by the action of phosphorus pentachloride on its *sodium* salt at 140—150°; the corresponding 1-*ethylbenzene*-2 : 4-*disulphonamide*, $C_6H_3Et(SO_2\cdot NH_2)_2$, m. p. 186—190°, was obtained from the chloride by the action of warm aqueous ammonia. On reduction with tin and hydrochloric acid, the acid chloride is converted into 2 : 4-*dithiol*-1-*ethylbenzene*, $C_6H_3Et(SH)_2$, an oil, b. p. 150—152°/18—20 mm., which reacts with alkaline methyl sulphate,

yielding 2 : 4-*dimethylthiol*-1-*ethylbenzene*, $C_6H_3Et(SMe)_2$, a pale yellow oil, b. p. 171—173°/14 mm., whilst with ethyl chloroformate and methyl chloroformate in the presence of alkali the products are colourless 2 : 4-*diethylthiocarbonato*-1-*ethylbenzene*, $C_6H_3Et(S·CO_2Et)_2$, b. p. 224—226°/14 mm., and the corresponding 2 : 4-*methyldithiocarbonato*-1-*ethyl benzene*, $C_6H_3Et(S·CO_2Me)_2$, a colourless oil, b. p. 217—220°/18 mm., respectively; the dithiol compound also reacts with chloroacetic acid in the presence of alkali and with picryl chloride, yielding, respectively, 1-*ethyl-benzene*-2 : 4-*dithiolacetic acid*, $C_6H_3Et(S·CH_2·CO_2H)_2$, colourless crystals, m. p. 137—140°, and 2 : 4-*dipicrylthiol*-1-*ethylbenzene*, $C_6H_3Et[S·C_6H_2(NO_2)_3]_2$, yellow needles, m. p. 197·5—199°; when heated with sodium acetate and acetic anhydride, the dithiol compound is converted into the *diacetyl* derivative, $C_6H_3Et(SAc)_2$, b. p. 218—220°/18 mm., and in the presence of alcoholic ammonia is oxidised by concentrated hydrogen peroxide with formation of a *substance*, $(C_6H_3EtS_2)_n$. Nitric acid in the cold converts 2 : 4-dimethylthiol-1-ethylbenzene into 5-*nitro*-2 : 4-*dimethylthiol*-1-*ethylbenzene*, $NO_2·C_6H_2Et(SMe)_2$, yellow, silky needles, m. p. 117—118°, whereas fuming nitric acid effects an oxidation to a *monosulphoxide* of the last product, $NO_2·C_6H_2Et(SMe)·SMeO$, yellow, silky needles, m. p. 119·5—120·5°.

In a similar manner to the preceding, 1-ethylbenzene-4-sulphonyl chloride was made to yield 4-*thiol*-1-*ethylbenzene*, $C_6H_4Et·SH$, b. p. 91—93°/12—13 mm. (*acetyl* derivative, $C_6H_4Et·SAc$, b. p. 136·5—140°/13—14 mm.), which in alkaline solution reacts with chloroacetic acid, giving 1-*ethylbenzene*-4-*thiolacetic acid*, $C_6H_4Et·S·CH_2·CO_2H$, colourless, silky needles, m. p. 61—67°, and in alcoholic solution with picryl chloride, forming 4-*picrylthiol*-1-*ethylbenzene*, $C_6H_4Et·S·C_6H_2(NO_2)_3$, deep yellow, silky needles, m. p. 113·5—116°.

By treating phenol with fuming sulphuric acid, a mixture of sulphonic acids can be obtained which, on conversion into the corresponding sodium or potassium salts and heating with phosphorus pentachloride at 140—150°, yields a more soluble (in ether) 4-*chlorobenzene*-1 : 3-*disulphonyl chloride*, $C_6H_3Cl(SO_2Cl)_2$, needles, m. p. 87—88°, and a less soluble 2-*chlorobenzene*-1 : 3 : 5-*trisulphonyl chloride*, $C_6H_2Cl(SO_2Cl)_3$, pale yellow needles, m. p. 170—171°. The former product on reduction with tin and hydrochloric acid gives 4-*chloro*-1 : 3-*dithiolbenzene*, $C_6H_3Cl(SH)_2$, a pale yellow liquid, b. p. 145—146°/13—14 mm. (*acetyl* derivative, $C_6H_3Cl(SAc)_2$, b. p. 214—217°/19 mm; *picryl* derivative, $C_6H_3Cl[S·C_6H_2(NO_2)_3]_2$, golden-yellow platelets, m. p. 201—204°; *dimethyl* derivative, $C_6H_3Cl(SMe)_2$, pale yellow oil, b. p. 177—179°/18 mm.; 4-*chlorobenzene*-1 : 3-*dithiolacetic acid*,

$$C_6H_3Cl(S·CH_2·CO_2H)_2,$$

silky needles, m. p. 159—160°; the reaction with ethyl chlorocarbonate followed an unusual course, the product under normal conditions consisting of 4-*chloro*-3(?)-*thiol*-1(?)-*ethylthiocarbonato-benzene*, $SH·C_6H_3Cl·S·CO_2Et$, b. p. 204°/18 mm., the completely

substituted 4-*chloro*-1 : 3-*diethylthiocarbonatobenzene*,

$$C_6H_3Cl(S \cdot CO_2Et)_2,$$
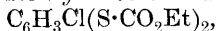
needles, m. p. 48—49°, being obtained only with the use of an excess of ethyl chlorocarbonate. The reduction of 2-chlorobenzene-1 : 3 : 5-trisulphonyl chloride gave 2-*chloro*-1 : 3 : 5-*trithiolbenzene*, $C_6H_2Cl(SH)_3$, yellow crystals, m. p. 64—67°; *methyl* derivative, $C_6H_2Cl(SMe)_3$, needles, m. p. 92—94°; 2-*chlorobenzene*-1 : 3 : 5-*trithiolacetic acid*, $C_6H_2Cl(S \cdot CH_2 \cdot CO_2H)_3$, colourless needles, m. p. 199—200°.   D. F. T.

Energetic Oxidation of Cholesterol by Nitric Acid. ADOLF WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **102**, 160—165).—The following compounds have been recognised among the products of the oxidation of cholesterol by nitric acid : dinitro*iso*propane and acetic, succinic, methylsuccinic, and α-methylglutaric acids. Acetone, hydroxy*iso*butyric acid, methyl *iso*hexyl ketone, and octane have previously been obtained, and the author points out that all these substances may be regarded as derived from an *iso*-octyl side-chain in cholesterol. On this assumption, cholesterol may be represented by the formula

$$CHMe \cdot CH_2 \cdot CH_2$$
$$CH_2 \cdot CH\text{———}CH \cdot CH \cdot CH_2 \cdot CHMe \cdot [CH_2]_3 \cdot CHMe_2 \ .$$
$$CH_2 \cdot CH\text{———}CH \cdot CH \cdot CH_2$$
$$CH_2 \cdot CH(OH) \cdot CH \cdot CH \vcentcolon CH$$

H. W. B.
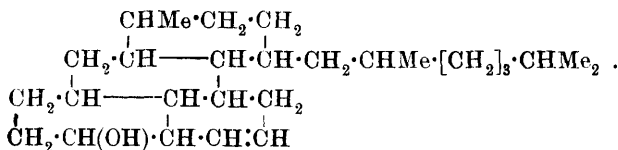
[Preparation of β-Diethylamino-α-phenylpropyl Benzoate and β-Ethylamino-α-phenylpropyl Benzoate.] NAGAYOSHI NAGAI (Brit. Pat. 117486, 1917).—The preparation of two new bases possessing local anæsthetic properties from β-amino-α-phenyl-propanol ("mydriatin," Jap. Pat. 27056) is described. Mydriatin is converted into a mixture of its mono- and di-ethyl derivatives by treatment with an ethyl haloid, and the ethyl derivatives are dissolved in ether and benzoylated. The ethereal solution of the benzoyl compounds is shaken with dilute hydrochloric acid, and the aqueous and ethereal layers are separated. From the aqueous layer by evaporation under diminished pressure, β-*diethylamino-α-phenylpropyl benzoate* ("*allocain S*"), $NEt_2 \cdot CHMe \cdot CHPh \cdot OBz$, is obtained as hydrochloride in the form of a colourless, transparent, vitreous mass. The ethereal solution contains *N*-benzoylethyl-mydriatin. It is evaporated, the residue heated with 30% hydrochloric acid, diluted, filtered, shaken with ether, and the separated aqueous layer filtered and evaporated, whereon β-*ethylamino-α-phenylpropyl benzoate hydrochloride* ("*allocain A*"),

$$NHEt \cdot CHMe \cdot CHPh \cdot OBz, HCl,$$
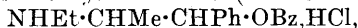
separates in flat needles. It is stated that benzoic esters of mono-and di-alkyl or mono- and di-aryl derivatives of mydriatin, and benzoic esters of aminophenyl alcohols homologous to mydriatin,

and of their alkyl or aryl derivatives, all possess more or less marked anæsthetic properties. A. S.

Coloured Acid Additive Products of Unsaturated Ketones.
FRITZ STRAUS [with HUGO BLANKENHORN] (*Annalen*, 1918, **415**, 232—256).—Mylo has shown (A., 1912, i, 4) that the acetals of aldehydes react with phosphorus pentachloride, thionyl chloride, etc., an alkyloxy-group being replaced by a chlorine atom. It is now shown that the acetals of certain unsaturated ketones in benzene solution react with hydrogen chloride or, better, phosphorus pentachloride (1 mol.) in the same way; the products are isolated in the form of the yellow or orange-red complex compound with phosphorus pentachloride or mercuric chloride. Thus the acetal of phenyl cinnamylidene methyl ketone in benzene solution is treated with phosphorus pentachloride (1 mol.) dissolved in the same solvent, and to the cooled, clear, faintly coloured solution is added drop by drop, with complete exclusion of moisture, a solution of mercuric chloride in dry ether, whereby the additive compound, $CHPh\!:\!CH\cdot CH\!:\!CH\cdot CPhCl\cdot OMe,HgCl_2$, m. p. about 110° (decomp.), is precipitated as a red oil, which rapidly solidifies and becomes crystalline. In a similar way, the *acetal* of phenyl styryl ketone, $CHPh\!:\!CH\cdot CPh(OMe)_2$, colourless needles, m. p. 46—46·5°, yields the *substance*, $CHPh\!:\!CH\cdot CPhCl\cdot OMe,HgCl_2$, yellow crystals, m. p. about 100° (decomp.), the *acetal* of pp'-dimethoxybenzophenone, colourless needles, m. p. 107—108°, yields the *substance*, $OMe\cdot CCl(C_6H_4\cdot OMe)_2,HgCl_2$, yellow, apparently amorphous powder, and the acetal of benzophenone yields the *substance*, $2CPh_2Cl\cdot OMe,5HgCl_2$, almost colourless needles. These substances are converted into the original ketones by hydroxylic solvents, into the original acetals by alcoholic sodium methoxide, and evolve methyl chloride when heated.

The bearing of the preceding substances on the constitution of the coloured acid additive compounds of the ketones is discussed.

The following substances are described: *p-chlorophenyl* p-*methoxystyryl* *ketone*, $OMe\cdot C_6H_4\cdot CH\!:\!CH\cdot CO\cdot C_6H_4Cl$, yellow needles, m. p. 121—122°, prepared from anisaldehyde and *p*-chloroacetophenone in aqueous alcohol containing about 0·5% of sodium hydroxide; p-*anisyl* p-*chlorostyryl* *ketone*, pale yellow crystals, m. p. 130—131°; p-*anisyl* p-*chlorocinnamylidenemethyl* *ketone*, yellow needles, m. p. 140°; p-*chlorophenyl* p-*methoxycinnamylidenemethyl* *ketone*, golden-yellow needles, m. p. 156°; and p-*chlorodistyryl* *ketone*, pale yellow needles, m. p. 134°. C. S.

The Quinonoid Oxidation Product of Methylene-di-β-naphthol.
MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1918, **39**, 299—306).—The yellow quinonoid oxidation product of methylenedi-β-naphthol was regarded by Abel (A., 1893, i, 172) as having the peroxide structure, $C_{10}H_6\!\!<\!\!^{CH_2}_{O_2}\!\!>\!\!C_{10}H_6$, but the o-quinonoid formula, $CH\!\!<\!\!^{C_6H_4-}_{CH\cdot CO}\!\!>\!\!C\!:\!CH\cdot CH\!\!<\!\!^{C_6H_4-}_{CO\cdot CH}\!\!>\!\!CH$, is

now proposed. This structure is in accordance with the formation of a *phenylhydrazone*, $C_{27}H_{20}ON_2$, orange-red needles, m. p. 153—156°, only the orthoquinonoid carbonyl group reacting with the usual reagents for ketonic substances; the phenylhydrazone on reduction with zinc and alcoholic acetic acid yields a *dihydro-*derivative, $C_{27}H_{22}ON_2$, a colourless powder, m. p. 133—136°; this derivative is probably a hydrazo-compound, whilst the parent phenylhydrazone is of azo-structure. With magnesium methyl iodide, the quinonoid compound reacts, forming a *substance*, $C_{22}H_{18}O_2$, probably $CH{<}^{C_6H_4}_{CH\cdot CMe(OH)}{>}C{:}CH\cdot CH{<}^{C_6H_4}_{CO\cdot CH}{>}CH$

needles, m. p. 135—145°, and with magnesium phenyl bromide an analogous derivative, $C_{27}H_{20}O_2$, probably

$$CH{<}^{C_6H_4}_{CH\cdot CPh(OH)}{>}CH{:}CH\cdot CH{<}^{C_6H_4}_{CO\cdot CH}{>}CH,$$
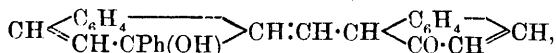
prisms, m. p. 130—170°, is obtained. Methyl sulphate converts methylenedi-β-naphthol into the *dimethyl* ether, $C_{23}H_{20}O_2$, leaflets, m. p. 144—147°.   D. F. T.

cis-trans.-**Isomerism in the Terpene Series. Addition of Hypochlorous Acid to Terpineol.** K. SŁAWIŃSKI (*Chemik Polski*, 1917, **15**, 97—105; from *Chem. Zentr.*, 1918, i, 920—921). —Terpineol dissolved in acetic acid was treated with sodium hypochlorite solution (1%); the product could be separated by fractional crystallisation into two portions: (1) m. p. 114—115°, b. p. 162—165°/15 mm., and (2) m. p. 60—80°, b. p. 125—155°, both of which consisted of the chlorohydrin of menthane-1 : 2 : 8-triol. The crude substance was treated with potassium hydroxide (20%) and the product separated into a liquid and a solid portion (m. p. 118—118·5°). The former, on distillation, yielded small quantities of pinol and pinol hydrate (annexed formula), which could only be derived from the *cis*-chlorohydrin of menthane-1 : 2 : 8-triol. From the fraction, b. p. 175—180°/13 mm , it was found possible to isolate *cis*-menthane-1 : 2 : 8-triol, m. p. 118—118·5°. The chlorohydrin of menthanetriol of m. p. 114—115° yielded almost exclusively pinol hydrate when treated with potassium hydroxide (20%), so that the chlorine atom must be attached to the carbon atom in position 6. From the mixture of chlorohydrins, m. p. 60—80°, only small amounts of the menthanetriol, m. p. 116—117·5°, could be isolated. The glycerol compound is therefore formed from the chlorohydrin of lower m. p.   H. W.
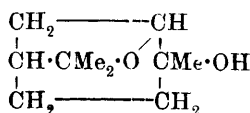
$$\begin{array}{ll} CH_2\text{———}CH & \\ |\qquad\qquad {}^{/}| & \\ CH\cdot CMe_2\cdot O\ \ CMe\cdot OH & \\ |\qquad\qquad\quad | & \\ CH_2\text{———}CH_2 & \end{array}$$

Constituents of Resins. II. Constituents of SumatraGum Benzoin. HANS LIEB and ALOIS ZINKE (*Monatsh.*, 1918, **39**, 219—230). —Unlike Siamese gum benzoin, Sumatra gum benzoin dissolves completely in hot dilute aqueous sodium hydroxide; the resulting solution, on boiling, deposits the *sodium* salt of l-*benzoresinol*,

m. p. 339—341°, $[\alpha]_D^{--}$ $-12\cdot88°$, probably of the composition $C_{29}H_{44}O_4$. The mother liquors on the addition of a little ether deposit the *sodium* salt (needles with $4H_2O$) of d-*sumaresinol*, $C_{30}H_{48}O_4,H_2O$, m. p. 298—299°, $[\alpha]_D^{2°}+51\cdot60°$ (*methyl* ether, crystals, m. p. 215—216°; *ethyl* ether, needles, m. p. 207—208°), isomeric with siaresinol (this vol., i, 398). The benzoresinol of Lüdy (A., 1893, i, 480, 666) was probably a mixture of d-suma-resinol with *l*-benzoresinol. **D. F. T.**

Vulcanisation without Sulphur by Ostromyslenski's Method. E. BUNSCHOTEN (*Kolloid Zeitsch.*, 1918, **23**, [i], 25—31). —Nitrobenzene and *m*-dinitrobenzene alone have little vulcanising action on rubber, and such organic accelerators as *p*-nitrosodi-methylaniline have no effect. Metallic oxides, however, act as strong catalysts, particularly lead oxide, which was used for all the experiments recorded. The rate of vulcanisation by *m*-dinitro-benzene depends on the sample of rubber used, and is increased by increasing the amount of catalyst or by increasing the temperature within the limits studied, 137—157°. The optimum time of heat-ing varies as the other factors are varied, but if it is exceeded, the physical properties of the product deteriorate. Samples of rubber vulcanised with dinitrobenzene rapidly deteriorate, and white crystals of unchanged dinitrobenzene make their appearance on the surface.

The viscosity of benzene solutions of rubber is increased by addi-tion of dinitrobenzene in the dark, particularly at high tempera-tures, but in the light the viscosity rapidly falls off. The opinion is expressed that the vulcanising action of such substances as *m*-dinitrobenzene is due to acceleration of polymerisation of the rubber. Sulphur acts in the same manner, but at the same time enters into combination with the rubber.

When rubber is heated with such inorganic oxidising agents as potassium permanganate, persulphate, dichromate, chlorate, nitrate, arsenic acid, bleaching powder, or manganese dioxide, incipient vulcanisation sets in, but the product is still soluble in benzene after long standing. [See also *J. Soc. Chem. Ind.*, 665A.]

E. H. R.

Scoparin. J. HERZIG and GERTRUD TIRING (*Monatsh.*, 1918, **39**, 253—267).—Goldschmiedt and von Hemmelmayr (A., 1893, i, 601; 1894, i, 542) have shown that scoparin, obtained from *Spartium scoparium*, contains a methoxyl group and six hydroxyl radicles, and attributed to the substance the formula $C_{20}H_{20}O_{10}$; it was found possible to alkylate only one hydroxyl radicle. By using diazomethane, however, it is possible to obtain a *dimethyl* derivative (*trimethyl*norscoparin), $C_{24}H_{28}O_{12}$, yellow crystals, m. p. 260—265° (decomp.), and a *trimethyl* derivative (*tetramethyl*nor-*scoparin*), $C_{25}H_{30}O_{12}$, yellow crystals, m. p. 220—238°, together with an amorphous *substance*. With methyl iodide and silver

oxide, it is possible to convert scoparin into a crystalline *octamethyl*nor*scoparin*, $C_{21}H_{12}O_3(OMe)_8$, m. p. 120—130°, with subsequent resolidification and m. p. 229—233°. The composition of these substances, as also that of acetylscoparin, renders it probable that the molecular formula of scoparin is not $C_{20}H_{20}O_{10}$, but $C_{22}H_{22}O_{11}$ (compare also Stenhouse, *Annalen*, 1851, **78**, 15.)

<div align="right">D. F. T.</div>

Synthesis of Alcohols in the Thiophen Series. V. THOMAS and V. COUDERC (*Bull. Soc. chim.*, 1918, [iv], **23**, 326—328).— Magnesium thienyl iodide reacts with ketones, giving thiophenic alcohols, of which the following have been prepared.

Diphenylthienylcarbinol, $HO \cdot CPh_2 \cdot C_4H_3S$, which apparently condenses with aniline hydrochloride, giving a *compound*, colourless leaflets.

Phenyldithienylcarbinol, $HO \cdot CPh(C_4H_3S)_2$, m. p. 90°. With benzil, a *compound* [*thienylphenylbenzoin*?,

$$C_4H_3S \cdot CPh(OH) \cdot COPh],$$
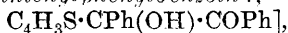
m. p. 56°, was obtained.

<div align="right">W. G.</div>

Eserine (Physostigmine). J. HERZIG and HANS LIEB (*Monatsh.*, 1918, **39**, 285—292).—The ordinary method for the determination of imino-methyl in eserine gives a result indicating the presence of two such groups, whereas the compound obtained after the removal of two methyl radicles, when examined by the micro-method, shows the presence of a third methyl group (Herzig and Meyer, this vol., i, 383; Straus, A., 1914, i, 78; 1915, i, 448); eseroline, when examined by the micro-method, also gives results almost twice as high for imino-methyl as by the macro-method (Straus, A., 1915, i, 448). This difference appears to be due to the larger proportion of hydriodic acid used in the micro-method, and if in the macro-method only 0·1 gram of eserine is taken to 20 c.c. of hydriodic acid, the result agrees with the presence of three imino-methyl groups. The reason of this peculiarity of eserine is at present undecided, although the possibility that the third and resistant radicle is an ethyl group, and not a methyl, receives some support from the behaviour of eserine when examined by Kirpal and Bühn's method for methyl determination (A., 1914, ii. 497; 1916, ii, 154).

<div align="right">D. F. T.</div>

The Alkaloids of the Calabar Bean. VII. Degradation by successive Iodomethylations of the Nuclei of Eserine and Geneserine. MAX POLONOVSKI and MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1918, [iv], **23**, 335—356. Compare A., 1915, i, 891, 892). —Eserethole methiodide (*loc. cit.*), when decomposed in aqueous solution with sodium carbonate, yields *eseretholemethine*, prisms, m. p. 80°, $[a]_D + 10°$, which gives a *hydriodide*, m. p. 170°, a *hydrochloride*, and a *zincochloride*, m. p. 193°. It is a tertiary base and gives a quaternary *methiodide*, m. p. 100°, $[a]_D - 11·8°$, which when decomposed with aqueous potassium hydroxide yields

trimethylamine and a new base, *etheserolene*, $C_{12}H_{12}N \cdot OEt$, an oil, giving an oily *bromo*-derivative and a crystalline *nitro*-derivative.

With methyl iodide, geneserine gives three compounds, one of which, m. p. 215° (*loc. cit.*), previously described as a methiodide, is really *ψ-geneserinemethine hydriodide*, from which the free *base* is obtained as an uncrystallisable syrup, giving a *methiodide*, m. p. 160° (decomp.), $[\alpha]_D -15°$. This methiodide is also one of the products of iodomethylation of geneserine, and when decomposed by alkalis yields methylamine and *ψ-geneserolenemethine methiodide*, m. p. 261°. The hydriodide, m. p. 215°, described above, when saponified by alkalis, yields *ψ-geneserolenemethine*, m. p. 171°, $[\alpha]_D -46°$, giving a *hydriodide*, m. p. 234°. With ethyl toluenesulphonate, it yields *ψ-geneseretholemethine*, and on acetylation gives *acetylgeneserolenemethine*, of which the *methiodide* has m. p. 175°. The methiodides of ψ-geneserinemethine or ψ-geneserolenemethine when treated with sodium hydroxide yield *ψ-geneserolene*, $HO \cdot C_{12}H_{12}ON$, m. p. 215°.

Eserine methiodide is converted by the action of hydrogen peroxide into ψ-geneserinemethine, and, similarly, eserethole yields *ψ-geneseretholemethine*, giving a *hydriodide*, m. p. 212°, and a *methiodide*, m. p. 130—140°.   W. G.

The Alkaloids of the Calabar Bean. VIII. Hydrogenation in the Eserine, Geneserine, and ψ-Geneserine Series.
MAX POLONOVSKI (*Bull. Soc. chim.*, 1918, [iv], **23**, 356—361).— Eserine and a number of its derivatives, when reduced by zinc and hydrochloric acid, yield dihydro-derivatives, the following being described.

Neither *dihydroeserine* nor its salts crystallise readily, but a *picrate*, m. p. 100°, was obtained.

Dihydroeseroline, m. p. 140°, gave a *picrate* and a *zincochloride*, m. p. 194°, $[\alpha]_D -95°$.

Dihydroeserethole, an oil, gave a *zincochloride*, m. p. 252°.

Dihydroeseretholemethine, an oil, gave a *zincochloride*, m. p. 242°, and a *methiodide*, m. p. 127°.

Geneserine and its derivatives on reduction gave, first, the corresponding eserine derivatives, and then their dihydro-derivatives.

Eserine methiodide when reduced by zinc and hydrochloric acid in alcoholic solution gave *dihydroeserinemethine*, m. p. 125°, $[\alpha]_D +11°$, which gave a *zincochloride*, m. p. 160°, and a *methiodide*. Eseroline methiodide similarly gave *dihydroeserolinemethine*, m. p. 128—129°.   W. G.

Dihydrophenazine and Dihydroacridine.
ROLAND SCHOLL [with W. NEUBERGER] (*Monatsh.*, 1918, **39**, 238).—Dihydrophenazine and dihydroacridine are formed when phenazine and acridine, respectively, in hot alcoholic solution are gradually introduced into an aqueous-alcoholic alkaline solution of sodium hyposulphite.   D. F. T.

Tetramethyl - 3 : 3′ - diaminodiphenylmethane. Roland
Scholl [with Jos. Lenko] (*Monatsh.*, 1918, **39**, 236—237).—When
heated with methyl iodide and methyl alcohol at 140—150°,
3 : 3′-diaminodiphenylmethane is converted into the *methiodide*,
$C_{19}H_{28}N_2I_2$, needles, m. p. 165°, of *tetramethyl*-3 : 3′-*diaminodi-
phenylmethane*, $C_{17}H_{22}N_2$, the oily, free base being obtainable by
heating the methiodide with soda-lime in an atmosphere of hydrogen
or with concentrated aqueous ammonia in a sealed tube at
180—190°.   D. F. T.

Hydrazino-acids. I. August Darapsky (*J. pr. Chem.*, 1917,
[ii], **96**, 251—327).—This communication opens with a general
review of the subject and a theoretical discussion of the new
results, which are grouped under three headings.

I. Reduction of the Hydrazone of Pyruvic Acid and the
Hydrazone and Azine of Phenylglyoxylic Acid, pp. 273—280
[with Moreshwar Prabhakar].—The hydrazine salt of pyruvic
acid hydrazone, $NH_2 \cdot N{:}CMe \cdot CO_2H, N_2H_4$ (Curtius and Lang, A.,
1891, 452), is reduced by means of sodium amalgam, the product
is evaporated to dryness with hydrochloric acid, and then esterified,
when the *hydrochloride* of ethyl α-*hydrazinopropionate*,

$$CO_2Et \cdot CHMe \cdot N_2H_3, HCl,$$

is obtained in white leaflets, m. p. 108—110° (decomp.). This is
identified by conversion into the free acid and its benzylidene com-
pound (Traube and Longinescu, A., 1896, i, 340; Thiele and Bailey,
A., 1899, i, 169).

Phenylglyoxylic acid, which is conveniently prepared by oxidising
mandelic acid with alkaline permanganate, reacts with alcoholic
hydrazine hydrate to give the *hydrazine* salt of *phenylglyoxylic acid
hydrazone*, $NH_2 \cdot N{:}CPh \cdot CO_2H, N_2H_4$, which crystallises in long
needles, m. p. 160—161°, and yields hydrazinophenylacetic acid
on reduction with sodium amalgam (see below).   The salt also
changes into the azine of phenylglyoxylic acid, $N_2({:}CPh \cdot CO_2H)_2$
(Bouveault, A., 1898, i, 585), when mixed with hydrochloric acid,
and the same product may be obtained by warming phenylglyoxylic
acid with hydrazine sulphate solution.   The azine yields *hydrazo-
phenylacetic acid*, $N_2H_2(CHPh \cdot CO_2H)_2$, m. p. 160—161°, on reduc-
tion with sodium amalgam, and this gives an *ethyl* ester, slender
needles, m. p. 88—89°.

II. Action of Hydrazine Hydrate on Bromoacetic, α-Bromo-
propionic, α-Bromoisovaleric, Bromomalonic, and Bromophenyl-
acetic Acids, pp. 280—300 [with Moreshwar Prabhakar].—The
hydrochlorides of ethyl hydrazinoacetate (Traube and Hoffa, A.,
1898, i, 235) and ethyl α-hydrazinopropionate (above) may be pre-
pared by boiling together alcoholic solutions of hydrazine hydrate
and the corresponding bromo-acids, and then saturating the mix-
tures with hydrogen chloride.   α-*Hydrazino*isovaleric acid,

$$N_2H_3 \cdot CHPr^\beta \cdot CO_2H,$$

separates in sparingly soluble leaflets, m. p. 230—235° (decomp.),

when hydrazine hydrate and α-bromoisovaleric acid are boiled together in alcohol; it forms a *benzylidene* compound, m. p. 121°, and a *diacetyl* derivative, m. p. 205°. Bromomalonic acid gives the *dihydrazine* salt of *hydrazinodimalonic acid*,

$$NH_2 \cdot N[CH(CO_2H)_2, N_2H_4]_2,$$
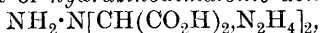
in long, pale yellow needles, m. p. 209° (decomp.). Bromophenyl-acetic acid (from mandelic acid and hydrobromic acid) yields *hydrazinophenylacetic acid*, $N_2H_3 \cdot CHPh \cdot CO_2H$ (above), in white leaflets, m. p. 189—190° (decomp.). This forms a *benzylidene* compound, m. p. 150°, a *salicylidene* compound, m. p. 153—154°, and a *dibenzoyl* derivative, m. p. 169·5—170°. It is oxidised by ferric chloride to benzaldazine and hydrazine chloride, and is converted into chloro- and bromo-phenylacetic acids by means of the halogens, and into mandelic acid by means of nitrous acid. The *ethyl* ester is an insoluble, yellow oil, which forms a *hydrochloride*, m. p. 138° (decomp.), a *hydrobromide*, m. p. 142·5°, and a *salicyl-idene* compound, slender, pale yellow needles, m. p. 107°, and reacts with chlorine to give ethyl chlorophenylacetate. The *methyl* ester also yields a *hydrochloride*, m. p. 148—148·5°. The salts of the esters react with potassium cyanate to give esters of *carbamylhydrazinophenylacetic acid*, $NH_2 \cdot CO \cdot N(NH_2) \cdot CHPh \cdot CO_2R$. The *ethyl* ester has m. p. 102·5—103°, and forms a *hydrochloride*, m. p. 153°, and *salicylidene* compound, m. p. 149·5°. The *methyl* ester has m. p. 141°. The hydrochloride of the ethyl ester also reacts with sodium nitrite to form *ethyl nitrosohydrazinophenyl-acetate*, $NH_2 \cdot N(NO) \cdot CHPh \cdot CO_2Et$, in silky needles, m. p. 59°, which gives the violet coloration with ferric chloride typical of nitrosohydrazines. This ester reacts with a further quantity of nitrous acid to give ethyl phenyldiazoacetate and then ethyl mandelate, decomposes at 110° into nitrous oxide and ethyl phenyl-glycine, and changes into ethyl triazophenylacetate,

$$N_3 \cdot CHPh \cdot CO_2Et$$
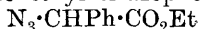
(Forster and Müller, T., 1910, **97**, 138), when distilled with 10% sulphuric acid.

III. ACTION OF HYDRAZINE HYDRATE ON α- AND β-BROMO-β-PHENYLPROPIONIC ACID, pp. 301—327 [with HERBERT BERGER].—α-Bromo-β-phenylpropionic acid is obtained as follows: ethyl benzylmalonate (Leuchs, A., 1911, i, 602) is hydrolysed by shaking it with an excess of potassium hydroxide (5 mols.), the free acid is then brominated in ethereal solution, and the bromobenzyl-malonic acid is heated at 125—130°. The acid is converted into α-hydrazino-β-phenylpropionic acid, $NH_2 \cdot NH \cdot CH(CH_2Ph) \cdot CO_2H$, by means of alcoholic hydrazine hydrate, and the product agrees with Traube and Longinescu's description *(loc. cit.)*. It forms a *hydrochloride*, benzylidene and salicylidene compounds *(ibid.)*, a *diacetyl* derivative, transparent tablets, m. p. 190—191°, a *dibenzoyl* derivative, rhombic needles, m. p. 190—192°, and it reacts with sodium nitrite and dilute sulphuric acid to give α-hydroxy-β-phenylpropionic acid (Fischer and Zemplén, A., 1910, i, 100). It also reacts with alcoholic hydrogen haloids to give the

hydrochloride (leaflets, m. p. 125°) and *hydrobromide* (snow-white leaflets, m. p. 123—125°) of the *ethyl* ester, this being a yellow oil, which changes when kept or heated (125°/14 mm.) into ethyl β-phenylpropionate. The hydrobromide yields *ethyl a-bromo-β-phenylpropionate*, b. p. 169°/14—15 mm., when treated with bromine in hydrobromic acid solution, whilst the hydrochloride may be converted into the p-*nitrobenzylidene* compound,

$$NO_2 \cdot C_6H_4 \cdot CH \colon N \cdot NH \cdot CH(CH_2Ph) \cdot CO_2Et,$$
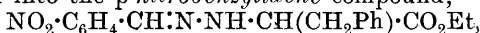
yellow rhombohedra, m. p. 87°, *ethyl a-semicarbazido-β-phenylpropionate*, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CH(CH_2Ph) \cdot CO_2Et$, needles, m. p. 147° (by means of potassium cyanate), and *ethyl a-nitrosohydrazino-β-phenylpropionate*, $NH_2 \cdot N(NO) \cdot CH(CH_2Ph) \cdot CO_2Et$, pale yellow, silky needles, m. p. 61° (by means of a concentrated solution of sodium nitrite). The nitroso-ester is decomposed by heat (115—120°) into nitrous oxide and the ethyl ester of phenylalanine, whilst on warming with dilute sulphuric acid it yields the *ethyl* ester (b. p. 154°/14 mm.) of *a-azido-β-phenylpropionic acid*, $CH_2Ph \cdot CHN_3 \cdot CO_2H$, this crystallising in large tablets, m. p. 24—27°, and forming an *ammonium* and a *silver* salt.

β-Bromo-β-phenylpropionic acid (from cinnamic acid and hydrogen bromide) reacts in quite another way with hydrazine hydrate. The product has the expected formula, but it is insoluble in alkalis and may be hydrolysed by hydrochloric acid. It is, in fact, *β-hydroxy-β-phenylpropionhydrazide*,

$$OH \cdot CHPh \cdot CH_2 \cdot CO \cdot NH \cdot NH_2,$$
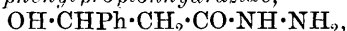
which crystallises in slender needles, m. p. 158°, and it is accompanied by some styrene and cinnamic acid. The hydrazide may also be prepared by the action of hydrazine hydrate on ethyl β-hydroxy-β-phenylpropionate (Findlay and Hickmans, T., 1909, **95**, 1009). It forms a *benzylidene* compound, glistening leaflets, m. p. 179°, and reacts with nitrous acid to give the *azide*,

$$OH \cdot CHPh \cdot CH_2 \cdot CO \cdot N_3,$$
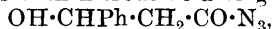
a pale yellow oil, which changes into *β-hydroxy-β-phenylpropionanilide*, m. p. 160°, when mixed with aniline.

It is mentioned that an alcoholic solution of hydrogen bromide can be obtained most readily by passing a current of dry hydrogen through warm bromine, then over platinised asbestos heated by a small flame, next through a tube containing red phosphorus, and finally into the alcohol. J. C. W.

The Methylation of Proteins. J. HERZIG and KARL LANDSTEINER (*Monatsh.*, 1918, **39**, 269—284. Compare A., 1914, i, 753).—In the earlier investigation, it was shown that for various proteins the action of diazomethane gives products containing a fairly uniform percentage of methyl radicle, as indicated by the figures 3·68—4·86% of methoxyl group and 3·72—5·34% of methyl attached to nitrogen; silk fibroin alone was exceptional, the product from this containing 2·79% of methoxyl and 4·93% of iminomethyl, even after repeated methylation. Wool, after being submitted repeatedly to the action of diazomethane, contains 5·89%

of methoxyl and 6·28% of imino-methyl. In a similar examination of the alcohol-soluble proteins from grain, it was found that the zein of maize is rather resistant to diazomethane, giving after several treatments a product containing 4·17% of methoxyl and only 2·9% of imino-methyl; gliadin from wheat is more reactive, and gives a product containing 7·06% of methoxyl and 2·56% of imino-methyl. Non-coagulated serum-albumin from the horse gives results similar to those obtained with the coagulated product (*loc. cit.*).

[With F. ZIPPERER and M. QUITTNER.]—A similar examination was made of the effect on proteins of a ten-hour treatment with a boiling 1% solution of hydrogen chloride in methyl alcohol; the products gave the following analytical results: silk fibroin, 1·4% of methoxyl, imino-methyl proportion almost identical with that of the original substance; wool, 3·80% of methoxyl, 1·49% of imino-methyl. With zein, and particularly with gliadin, the hydrogen chloride causes considerable hydrolysis, a similar result being also obtained in the treatment of Witte's peptone. The product from zein contains 5·47—6·18% of methoxyl, but the imino-methyl content is almost unaltered. With gliadin, a large proportion passes into solution, the undissolved residue, as well as the portion of the dissolved material precipitable by ether, containing approximately 7% of methoxyl; it is probable that the extent of the hydrolytic effect of the methyl-alcoholic acid is greater than these figures indicate, because the resulting glutamic acid is remarkably resistant to esterification by this reagent. It is also probable that to some extent esterification products formed in the earlier stages of the treatment undergo subsequent hydrolysis by the action of water resulting from the interaction of the hydrogen chloride and methyl alcohol. The product of the reaction between zein or gliadin and methyl-alcoholic hydrogen chloride on treatment with diazomethane undergoes a marked increase in methoxyl content, which, however, is probably due in part to the presence of phenolic groups.

D. F. T.

Legumin in Peas. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 85—104).—The legumin prepared from peas by extraction with salt solution and subsequent removal of the salt by dialysis (Osborne, A., 1896, i, 715) is soluble in dilute salt solutions, and thus differs from the insoluble legumin obtained from peas by extraction with water or dilute alkali, followed by precipitation with dilute acetic acid (Ritthausen, *J. pr. Chem.*, 1868, **103**), The author proposes to designate the former as *a*-legumin and the latter as *b*-legumin. *b*-Legumin appears to be an acid metaprotein. *a*-Legumin also forms a compound with acid, which, however, is not *b*-legumin, because the latter swells in water, giving a viscid, non-filterable solution, whereas the acid compound of *a*-legumin does not swell in water, but gives a limpid, milky emulsion which filters readily, yielding an opalescent filtrate. Other slight differences in the properties of *a*- and *b*-legumins are

described, which indicate that b-legumin is not formed from a-legumin by the action of acid, alkali, or water, but is a distinct protein.   H. W. B.

Hæmoglobin, Bilirubin, and Urobilinogen. W. C. DE GRAAFF (*Chem. Weekblad*, 1918, **15**, 1032—1045, 1059—1071).— A summary of the literature of the subject.   A. J. W.

Influence of Electrolytes on the Osmotic Pressure of Gelatin Solutions. JACQUES LOEB (*J. Biol. Chem.*, 1918, **35**, 497—508. Compare this vol., i, 413).—The osmotic pressures of solutions of gelatin which has been treated with acids, bases, and salts by the author's method (*loc. cit.*) are affected by the preliminary treatment which the gelatin has received in exactly the same way as the other properties so far examined, namely, swelling, viscosity, and resistance to precipitation by alcohol. The measurements were carried out by Lillie's method (A., 1907, ii, 847), and the results demonstrate that gelatin treated with neutral salts and bases with univalent cation and acids with univalent anion has a greater osmotic pressure when dissolved in water than a solution of untreated gelatin, whilst salts and bases with bivalent cation and acids with bivalent anion do not produce any effect on the gelatin.   H. W. B.

Action of Chymosin and Pepsin. V. Action of the Enzymes on Legumin from Peas. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 105—147. Compare this vol., i, 459). —Chymosin acts on other proteins besides caseinogen, forming albumoses. Acid- and alkali-legumin are hydrolysed by chymosin in neutral solutions or in the presence of so little acid that any pepsin present would exert no, or but very little, hydrolytic action. The results are considered by the author to support the theory that assigns a separate identity to chymosin and pepsin.   H. W. B.

New Salts of 1 : 1-Dimethylarsepedine. ENRIQUE V. ZAPPI and JUAN L. LANDABURU (*Bull. Soc. chim.*, 1918, [iv], **23**, 324—326. Compare A., 1916, i, 575, 683).—The salts were prepared by neutralising a solution of 1:1-dimethylarsepedine hydroxide (*loc. cit.*, i, 575) in the presence of phenolphthalein with the requisite acid, the solution being evaporated to dryness over sulphuric acid and sodium hydroxide.

1 : 1-*Dimethylarsepedine methochloride*,$CH_2 <^{CH_2 \cdot CH_2}_{CH_2 \cdot CH_2}> AsMe_2Cl$, has m. p. 237° (decomp.); the *methobromide*, m. p. 277—280° (decomp.).

1 : 1-*Dimethylarsepedine sulphate* has m. p. 232° (decomp.); the *nitrate*, m. p. 260° (decomp.); the *hydrogen carbonate*, $C_8H_{16}As,HCO_3$, m. p. 156—157° (decomp.).   W. G.

Physiological Chemistry.

The Haldane-Henderson Method for Estimating the Tension of Alveolar Carbon Dioxide and the Influence of Oxygen on the Stimulability of the Respiratory Centres. MOTOI YAMADA (*Biochem. Zeitsch.*, 1918, **89**, 27—47).—A new valve is described and figured for use with Henderson's modification of Haldane's method for estimating alveolar carbon dioxide. It was found that when the amount of carbon dioxide inhaled was greater than normal, the alveolar ventilation was better when the gas was mixed with pure oxygen than when mixed with air. Hence oxygen has a favourable influence on the breathing centre. No influence could be found to be exerted on the respiratory centre by the inhalation of pure oxygen. S. B. S.

The Influence of Atropine on Respiratory Metabolism and the Blood Gases. GEORG KELEMAN (*Biochem. Zeitsch.*, 1918, **89**, 338—349).—There is a marked diminution of the respiratory metabolism of dogs after intravenous injection of atropine, which effect can be antagonised by the simultaneous injection of pilocarpine. The increased gaseous metabolism produced by pilocarpine can be diminished by atropine, and the diminished gaseous metabolism produced by the latter alkaloid can be increased by the subsequent injection of the former. The content of the blood in carbon dioxide is diminished by injection of atropine. The diminished output of carbon dioxide produced by injection of atropine, already mentioned, is due, therefore, not to a diminished secretion of this gas by the lungs, but to a general diminution of its production. S. B. S.

The Action of Pilocarpine on Respiratory Metabolism and the Gas Content of the Blood. G. KELEMAN (*Biochem. Zeitsch.*, 1918, **89**, 135—155).—The increased secretory activity of the salivary glands produced by pilocarpine is accompanied by an increased metabolism of energy (about 10%). There is also produced at the same time an increased carbon dioxide content in the blood, both venous and arterial. There is no evidence, however, of an increased "secretion" of carbon dioxide by the blood. S. B. S.

The Agglutination of Red Blood Corpuscles and the Hofmeister Series. W. RADSMA (*Biochem. Zeitsch.*, 1918, **89**, 211—219).—Blood corpuscles, suspended in a large amount of isotonic solution of dextrose, readily agglutinate on addition of a small amount of a salt; 0·04% of sodium chloride is sufficient to bring about this phenomenon. The anions, in their activity as regards this agglutinative effect, follow the order of the Hofmeister series,

and this indicates that some hydrophil colloid plays a part in maintaining the stability of a suspension of the corpuscles.   S. B. S.

The Action of Chlorates on the Blood of Man and certain Animals. EGBERT CAESAR (*Biochem. Zeitsch.*, 1918, **89**, 1—26).— Details are given as to the concentrations in which potassium chlorate exerts an injurious action on the blood, giving rise to the formation of methæmoglobin. The general conclusion is drawn that potassium chlorate can act toxically when taken *per os*, and that it should not be used indiscriminately in tooth-powders and analogous preparations. The astringent action of aluminium chlorate is due to the aluminium ion. A detailed criticism is given of a commercial preparation of chlorates known as Mallebrein's.
S. B. S.

Clinical Value of Freezing-point Determinations. FRITZ EIGENBERGER (*Zeitsch. physiol. Chem.*, 1918, **102**, 166—175).— The addition of urea, dextrose, or sodium chloride to a colloidal solution of gelatin, starch, or blood-serum produces scarcely any lowering of the freezing point, measured by Beckmann's method. When an acid or an alkali is added, a considerable depression may be observed, but it does not equal the calculated value. The author draws the conclusion that the determination of the freezing point of a pathological serum is not likely to furnish any valuable clinical information.   H. W. B.

The Influence of Oxygen on Metabolism. I. Experiments on Meal-worms. TORBJÖRN GAARDER (*Biochem. Zeitsch.*, 1918, **89**, 48—93).—The metabolism of the *Tenebrio* chrysalis is independent of the oxygen tension of the atmosphere as long as the oxygen tension of the tissues is positive. As the oxygen tension of the atmosphere sinks, the gradient between the oxygen tension of the tissues and the atmosphere remains constant, until the former tension becomes zero. With further diminution of the tension of the oxygen of the atmosphere beyond this point, the gradient of oxygen tension between the tissue and atmosphere sinks, and the oxygen consumption of the chrysalis diminishes. Numerous numerical data are given in support of these statements, and the experiments were carried out by means of a modified micro-respirator of Krogh. If the chrysalis is allowed to remain in an atmosphere so poor in oxygen that the metabolism is sub-normal, certain anaerobic processes take place. On removing the animal to an atmosphere of normal oxygen content, the metabolism remains for some time sub-normal; it then increases and becomes greater than normal, and this is apparently due to the destruction of products formed during the anaerobic conditions.   S. B. S.

The Influence of Oxygen Tension on Metabolism. II. Experiments with Carp. TORBJORN GAARDER (*Biochem. Zeitsch.*, 1918, **89**, 94—125).—An apparatus is figured and described for

passing water with known oxygen content through the gills of fish and estimating the consumption. It is found that there is a very slow increase in oxygen consumption with increasing tension of the oxygen dissolved in water. The increase is so small that the conclusion is drawn that the changes in oxygen tension in water which take place normally are without any appreciable effect on the metabolism. There is a linear relationship between oxygen consumption and the oxygen tension of the water passing the gills, that is, the oxygen consumption is in accordance with laws governing the absorption of gases by a liquid, and the increase of the consumption can be explained by assuming that the oxygen dissolved physically in the blood is utilised. S. B. S.

Metabolism of Glycine given Intravenously at Constant Rates. JULIAN H. LEWIS (*J. Biol. Chem.*, 1918, **35**, 567—576).— Glycine can be injected intravenously into a dog at the rate of 0·2 gram per kilo. of body weight per hour without causing the appearance of the amino-acid in the urine. The nitrogen is subsequently excreted at a slower rate in the form of urea.
H. W. B.

Significance of Glycollic Acid, Glyoxal, Glycollaldehyde, and Aminoacetaldehyde in Intermediary Metabolism. ISIDOR GREENWALD (*J. Biol. Chem.*, 1918, **35**, 461—472).—The subcutaneous injection of glycollaldehyde and aminoacetaldehyde into phloridzinised dogs is followed in each case by an increased elimination of dextrose; similar injections of glyoxal or glycollic acid do not intensify the glycosuria. These results favour the view that glycine and dextrose are interchangeable in the organism in the following manner: glycine $\rightleftarrows$ aminoacetaldehyde $\rightleftarrows$ glycollaldehyde $\rightleftarrows$ dextrose. H. W. B.

Nuclein Metabolism. V. Destruction of the Purine Ring by Bacteria in the Human Intestine. S. J. THANNHAUSER and G. DORFMÜLLER (*Zeitsch. physiol. Chem.*, 1918, **102**, 148—159. Compare this vol., i, 47).—After twenty days' incubation of adenosine, guanosine, or inosine with a culture of bacteria from the human intestine, from 60 to 100% of the nitrogen in the nucleoside is found to have been converted into ammonia. These results are in harmony with and explain the observation that the purines in ingested nucleic acid are not quantitatively excreted in the form of uric acid, but to a certain extent undergo degradation in the body and are eliminated as urea (doubtless through the intermediate formation of ammonia by the action of the intestinal bacteria). H. W. B.

Fat soluble Vitamine. I. H. STEENBOCK, P. W. BOUTWELL, and HAZEL E. KENT (*J. Biol. Chem.*, 1918, **35**, 517—526).— Experiments on rats are described, the results of which indicate

that the fat-soluble vitamine in butter-fat is destroyed by heating the butter-fat at 100° for four hours.   H. W. B.

The Changes of Condition in Tissue Colloids Associated with the Healing of Wounds. W. VON GAZA (*Kolloid Zeitsch.*, 1918, **23**, [i], 1—11).—A discussion of the healing of wounds in the light of modern conceptions of colloid chemistry.   E. H. R.

Indicators in Animal Tissues. W. J. CROZIER (*J. Biol. Chem.*, 1918, **35**, 455—460. Compare A., 1916, ii, 337).—The hydrozoan *Velella velella*, L., contains a blue pigment which gives an orange extract with 70% alcohol. It is made bright orange by alkalis and decolorised by acids.

Two sponges, " A " and " B," members of the *Aplysinidæ*, have yielded coloured aqueous extracts; one is turned bright yellow by acids and blue to purple by alkalis; the other is a crimson-coloured extract, turned violet by acids and yellow by alkalis.

The anterior portion of the œsophagus of the large holothurian *Stichopus moebii*, Semp., contains a reddish-purple echinochrome which is not readily extracted from the tissue. Alkalis intensify the colour; acids change it to bright orange.

By comparing the colour of the natural tissue with the extracted pigment, it is possible to draw some conclusions regarding the degree of acidity or alkalinity of the tissue cells. The tissues of marine animals are in general more acid than the surrounding sea-water, the hydrogen-ion concentration varying between $p_H = 6·0$ and $p_H = 7·6$, and increasing when death ensues to $p_H = 5$ to 6. Higher alkalinity in the protoplasmic juices of young, rapidly growing individuals has never been observed in these pigmented animals, the normal reaction of the cells concerned being acid rather than alkaline.   H. W. B.

The Phosphorus in Organic Combination in Human Urine. Observation in Acute Yellow Atrophy of the Liver. JOH. FEIGL (*Biochem. Zeitsch.*, 1918, **89**, 126—134).—Chiefly a review of the literature and of methods.   S. B. S.

The Biochemical Behaviour of Aminomethyl Hydrogen Sulphite. E. SALKOWSKI (*Biochem. Zeitsch.*, 1918, **89**, 178—198).—Aminomethyl hydrogen sulphite, $NH_2 \cdot CH_2 \cdot O \cdot SO_2H$ (Reinking, Dehnel, and Labhardt, A., 1905, i, 261), yields formaldehyde in the distillate when an aqueous solution is distilled, and also, but very slowly, when it is kept in water at ordinary temperatures. Experiments with urine and meat indicate that it is of little value as an antiseptic. No formaldehyde could be detected in the urine after administration of the acid to a rabbit. When administered to a dog, part appears, from the increase of the neutral sulphur in the urine, to be excreted unchanged. Indican disappears from the urine during administration, and this fact seems to indicate that aminomethyl hydrogen sulphite acts as an intestinal antiseptic.   S. B. S.

The Photolytic and Photodynamic Action of an *a*-**Furo-**
β-**diazole.** P. R. Kögel (*Biochem. Zeitsch.*, 1918, **89**, 204—210).
—The substance employed was *β*-naphthoxadiazole-4-sulphonic
acid, which undergoes change on exposure to light. The photo-
dynamic effects were demonstrated on the protozoon *Colpidium
colpoda*.   S. B. S.

Physiological Action of Hydroatophan. Julius Pohl
(*Zeitsch. J. exper. Path. Ther.*, 1917, **19**, 198—204; from *Chem.
Zentr.*, 1918, i, 929).—Experiments on the frog show that the
action of the atophan molecule on the heart is completely altered
by hydrogenation and is replaced by a spinal and peripheral excita-
tion. Toxicity towards warm-blooded animals is characterised by
increased excitability of the spinal reflexes.   H. W.

**The Influence of Temperature on the Strength of Action
and Surface Activity of Narcotics.** Rudolf Unger (*Biochem.
Zeitsch.*, 1918, **89**, 238—278).—The influence of changes of
temperature on narcotic activity of various substances, such as
chloral hydrate, salicylamide, benzamide, monoacetin, and ethyl
alcohol, was investigated, the subjects of experiment used being
tadpoles, the fish *Leuciscus*, and the sciatic nerve of frogs. In
some cases, increase of temperature increased, and in others it
diminished narcotic activity. These changes could not always,
however, be correlated with changes in the distribution of the
narcotic between oil and water, as would follow from the Overton-
Meyer theory, or with the change in surface tensions of the solu-
tions. Account has to be taken in investigations of this character
of the effect of temperature changes on the general metabolic
activity.   S. B. S.

**Relation between the Chemical Structure of the Opium
Alkaloids and their Physiological Action on Smooth
Muscle with a Pharmacological and Therapeutic Study of
some Benzyl Esters. II. Pharmacological and Thera-
peutic Study of some Benzyl Esters.** David I. Macht (*J.
Pharm. Expt. Ther.*, 1918, **11**, 419—446. Compare this vol.,
i, 418).—Benzyl acetate and benzoate produce the same effects on
smooth muscle as papaverine, but are comparatively non-toxic;
they may therefore be employed clinically to alleviate conditions
of excessive peristalsis or spasms of viscera containing smooth
muscle fibres. Beneficial effects have been observed to follow the
administration of one or other of these esters in cases of chronic
diarrhœa, dysentery, asthma, etc.   H. W. B.

**Relations between the Constitution and the [Physio-
logical] Activity of** *ac*-**Tetrahydro-**β-**naphthylamine and its
Derivatives.** Ernst Waser (*Schweiz. Chem.-Zeit.*, 1917, **1**,
12—15; from *Chem. Zentr.*, 1918, i, 830).—Derivatives of *ac*-tetra-
hydro-β-naphthylamine have been examined with the object of

finding one having a quicker and more powerful fever-producing action than the base itself. Experiments undertaken to bring the base into an active, fever-producing form show that in this case Gros's theory, according to which the anæsthetic potential of a salt is proportional to its degree of hydrolytic dissociation, does not hold. There is no appreciable difference in the physiological activity of *ac*-tetrahydro-β-naphthylamine and its optically active modifications. The entrance of acyl groups produced a diminution of the activity instead of the expected increase. Whilst the acetyl derivative is much more poisonous to frogs, the converse is the case with warm-blooded creatures (dogs), in which the base itself produces strong dilatation of the pupil and increase of the temperature and the blood-pressure, whilst the acetyl derivative produces contraction of the pupil and a lowering of the temperature and the blood-pressure. A similar behaviour is also shown by the ·CHO, ·COPh, ·CO₂Et, ·CO·NHPh, ·CS·NHPh, and ·CS·NHEt derivatives. Of the alkyl derivatives, the monomethylated base serves the author's purpose, since in small doses it produces a relatively high feverishness in the shortest time. The ethyl derivative acts like *ac*-tetrahydro-β-naphthylamine itself. It has been found that *ac*-tetrahydro-β-naphthylamine produces complete immunity against any further injection of itself or of the methyl and ethyl derivatives, that the methyl derivative produces immunity against itself and the ethyl derivative, and that the latter only produces immunity against itself. *N*-Acyl-*N*-alkyl derivatives produce effects which are a combination of those of the mono-substituted derivatives. Thus injection into dogs of *N*-acetyl(or formyl)-*N*-methyl-*ac*-tetrahydro-β-naphthylamine produces on the one hand dilatation of the pupil (effect of the methyl derivative) and on the other a lowering of the temperature (effect of the acyl derivative). Experiment shows that a portion of the substance is hydrolysed in the organs (of warm-blooded animals); the resulting methyl derivative or *ac*-tetrahydro-β-naphthylamine itself suffices not only to suppress the myotic action of the acyl group, but even to reverse it, but is insufficient to influence the temperature effect. All the results are tabulated.   C. S.

Chemistry of Vegetable Physiology and Agriculture.

Problems of Bacteria Adsorption. H. BECHHOLD (*Kolloid Zeitsch.*, 1918, **23**, 35—43).—In the course of a research on the adsorption of bacteria by different materials, experiments were made on the adsorption of certain dyes by the same adsorbents. The basic dye, methylene-blue, was strongly adsorbed by a variety

of substances, such as animal and vegetable charcoal, fuller's earth, bolus, clay, permutite, and silicic acid, whilst trypan-blue, which is acidic, was adsorbed only by charcoal and ferric hydroxide. There is a strong resemblance between the relative adsorptive powers of the above materials for bacteria (*Staphylococcus* and *Bacterium coli*) and for methylene-blue, although ferric hydroxide adsorbs the bacteria and not the colour.   Charcoal and fuller's earth surpass any other adsorbent materials, although the mean diameter of their particles may be greater than that of the less adsorbent substances.   E. H. R.

The Catalase of Bacteria. MARTIN JACOBY (*Biochem. Zeitsch.*, 1918, **89**, 350—354).—The paper describes attempts to prepare a pure catalase. *Bacillus proteus* was grown on the medium already employed by the author, which contains, besides the inorganic salts, sodium aspartate and sodium lactate. From such cultures, an active catalase could be obtained by precipitation with ammonium sulphate, magnesium sulphate, and sodium chloride. The precipitate obtained was dissolved in water. A catalase could also be precipitated by mercuric chloride; in this case, an active preparation was obtained by redissolving the precipitate in potassium cyanide solution.   S. B. S.

Chemical Composition and Formation of Enzymes. XV. Further Experiments with Bacterium Acidi lactis (Streptococcus lactis). HANS EULER and OLOF SVANBERG (*Zeitsch. physiol. Chem.*, 1918, **102**, 176—184. Compare this vol., i, 55, and Euler and Griese, A., 1917, i, 679).—The lactic acid fermentation of lactose by *Streptococcus lactis* is not accelerated, but rather inhibited by sodium dihydrogen phosphate, and in these new experiments an evolution of carbon dioxide has not been observed. The difference between these results and those formerly described (*loc. cit.*), may be due to the employment of a different species of bacterium or to a contamination in the earlier experiments of the bacteria with yeast cells or other micro-organisms. The presence of sodium lactate appears to exert an inhibiting action on the formation of lactic acid by the bacteria.   H. W. B.

The Arrest of Alcoholic Fermentation in the Aldehyde Stage. An Experimental Confirmation of the Acetaldehyde Pyruvic Acid Theory. CARL NEUBERG and ELSA REINFURTH (*Biochem. Zeitsch.*, 1918, **89**, 365—414).—Neuberg has shown that yeast contains a ferment which decomposes pyruvic acid into acetaldehyde and carbon dioxide; furthermore, acetaldehyde is readily reduced during yeast fermentations to ethyl alcohol. It seemed therefore probable that acetaldehyde is an intermediate product in alcoholic fermentation. The authors now show that considerable amounts of acetaldehyde can be obtained in the ordinary yeast fermentations of sugars, and can be isolated if the fermentation is

carried out in the presence of sodium sulphite. The equations representing the reactions may be represented as follows:

(a) $C_6H_{12}O_6 + Na_2SO_3 + H_2O = C_6H_{12}O_5(OH)\cdot O\cdot SO_2Na + NaOH$.

(b) $\frac{1}{2}C_6H_{12}O_5(OH)\cdot O\cdot SO_2Na = H_2 + CH_3\cdot C(OH)(CO_2H)\cdot O\cdot SO_2Na$.

(c) $CH_3\cdot C(OH)(CO_2H)\cdot O\cdot SO_2Na_2 = CH_3\cdot CH(OH)\cdot O\cdot SO_2Na + CO_2$.

(d) $NaOH + CO_2 = NaHCO_3$.

As one-half of the molecule should yield aldehyde, which acts as acceptor for the hydrogen evolved, it should not be expected that one molecule of sugar should yield more than one molecule of carbon dioxide and one molecule of aldehyde.

$$C_6H_{12}O_6 = CH_3\cdot CHO + CO_2 + \left[\left. \frac{C_6H_{12}O_6}{2} \right\} H_2 \right].$$
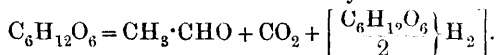
An amount of aldehyde equivalent to 73·45% obtainable on this theory has been obtained.

Full details are given of the methods employed for the quantitative estimation of the aldehyde and alcohol formed during fermentation.   S. B. S.

Willstätter's Researches on the Assimilation of Carbon Dioxide. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15,** 1138—1146). —A review of the recent work of Willstätter on this subject.

A. J. W.

The Physiological Significance of Potassium in Plants. TH. WEEVERS (*Biochem. Zeitsch.*, 1918, **89,** 281—282).—A final reply to Stoklasa (A., 1917, i, 682).   S. B. S.

Active Principles of the Horse Chestnut. GEORGES MASSON (*Bull. Sci. Pharmacol.*, 1918, **25,** 65—72; from *Chem. Zentr.*, 1918, ii, 40—41).—Separate examination of the seed capsules and cotyledons has led the author to revise his previous conclusions (*Diss.*, Paris, 1910).

The seed capsules yield, after extraction with alcohol, an almost fat-free, bright red residue which gives red needles when crystallised from water; the compound shows tannin reactions, and is transformed by warm sulphuric acid into gallic acid and a red substance.

From the fat-free cotyledons, two acids are obtained: (1) *Aesculic acid*, fine needles, m. p. 214—215°, which are insoluble in water. The salts are yellow and amorphous. The *barium, calcium, magnesium,* and *lead* salts were investigated. Protracted boiling of an alcoholic solution of the acid which has been treated with 5% sulphuric acid slowly causes hydrolysis with formation of a reducing sugar. (2) *Aesculinic acid,* goldenyellow, apparently crystalline needles, m. p. 230—231°, lævorotatory, soluble in water. The *alkali* and *barium* salts are yellow and soluble in water; their solutions have emulsifying properties. The *lead* salt is insoluble in water. The acid is hydrolysed, even by dilute acids, to a reducing sugar and a new *acid*. The reducing sugars produced from æsculic and æsculinic acids consist of a mixture of mannose and dextrose.

It appears, therefore, that the seed capsules contain a tannin yielding gallic acid. Two glucosidic saponins are present in the cotyledons, of which the insoluble æsculic acid is emulsified by the aqueous solutions of the æsculinic acid; the mixture of acids constitutes the active principle of the seeds, previously termed argyrescin or aphrodescin. If the whole fruit is examined, the presence of the gallic acid of the capsules causes the formation of tannin compounds having properties differing from those of the glucosides. H. W.

[**The Pigment of Myrtle Berries and its Use as an Indicator.**] C. MARINI (*Annali Chim. Appl.*, 1918, **10**, 32—36).— The pigment of myrtle berries (*Vaccinius myrtillus*, L.) appears to be identical with œnocyanin, the red colouring matter of wine, to which Glenard (*Ann. Chim. Phys.*, 1858, [iii], **54**, 369) assigned the formula $C_{20}H_9O_2$, the œnolic acid in which combines with bases to form salts. The pigment of myrtle berries may be extracted with 50% alcohol and precipitated with basic lead acetate. By digesting the washed and dried precipitate, first with ether saturated with hydrogen chloride, then with ether, and finally digesting the insoluble portion with alcohol, and treating the alcoholic extract with ether, a carmine-red pigment is precipitated. This consists of two components, one of which is insoluble in hot water, whilst the other, $C_{20}H_{14}O_{12}$, which predominates, is soluble in acidified water, and when boiled with acids is converted into the first component, with the elimination of dextrose. It thus appears to be a glucosidal compound, and is probably a gluco-tannoid. The pigment extracted from the berries with 90% alcohol acts as a weak acid and forms green salts with alkalis. Test papers, which are more sensitive than turmeric paper, may be prepared from it for use as indicators of acidity or alkalinity. C. A. M.

Pollen and Pollen Disease. I. Chemical Composition of Ragweed Pollen. JESSIE HORTON KOESSLER (*J. Biol. Chem.*, 1918, **35**, 415—424).—The pollen grains of ragweed (*Ambrosia artemisifolia* and *A. trifida*), which produce hay fever in certain susceptible persons, contain about 10·5% of water, 10·6% of mineral matter, and 78·9% of organic substances, including 7% of sugars, 10% of lipoids, consisting of fats and phytosterol, and 37% of proteins, crude fibre, etc. The dry pollen contains 4·7% of nitrogen. H. W. B.

Absorptive Power of Zeolitic Bases of Soil. K. K. GEDROITZ (Reprint, pp. 1—55).—Black soil has been treated with 0·2*N*-, *N*-, and 4*N*-solutions of a number of chlorides, both separately and together, this treatment being repeated until the bases were completely extracted; the results obtained are as follows.

All the zeolitic bases of a soil may be displaced by a certain cation. The bulk of these bases consists of lime (almost 75%), the remainder being magnesia (20%), soda, potash, and possibly manganese oxide. The extraction of soils with hydrochloric acid (about

10%) for the estimation of the zeolitic part gives certain results only for the zeolitic lime, the proportions of the other bases found being too high. Iron and aluminium do not occur in soils—even the red soils of Algeria—as zeolitic bases in detectable proportion.

All the zeolitic bases of a natural soil may be displaced completely by any base either ordinarily present or not in the soil. Except with soils not saturated by bases, the quantity of base absorbed is equivalent to the quantity of bases displaced from the zeolitic part of the soil.

Soil saturated by any base or bases contains this base or bases in the zeolitic part in such quantities as, expressed in equivalents, are independent of the nature of the bases.

The energy of absorption varies with different cations, and is greatest with tervalent and less with bivalent cations; calcium is absorbed more energetically than magnesium. Univalent cations are still more feebly absorbed, sodium more so than potassium.

The relation of the qualitative and quantitative composition of the zeolitic bases of soils to the life of the soil and plant and various other questions are discussed.   T. H. P.

Saline Soils and their Improvement. K. K. GEDROITZ (Reprint, pp. 1—16).—The author describes the treatment necessary for the improvement of soils (1) containing an excess of neutral salts, such as the so-called white alkali land, and (2) containing soda, such as the black alkali land.   T. H. P.

The Inversion of Cane-sugar by Soils and Allied Substances and the Nature of Soil Acidity. F. E. RICE and S. OSUGI (*Soil Science*, 1918, **5**, 333—358).—It is shown that soils of many kinds can cause the inversion of sucrose, this power being a property of the mineral portion as well as of the organic matter of the soil. This effect is due to acid, which may be present as a slight amount soluble in the sugar solution or in one of three insoluble forms: (*a*) acids ordinarily easily soluble, but in the soil strongly adsorbed on the soil particle surfaces; (*b*) an insoluble acid, such as silicic acid; (*c*) acid liberated from a neutral salt present in the soil solution by its breaking down, owing to the base being more strongly adsorbed than the acid, this being thus left free to cause inversion of the sugar. Many soils showed inverting action on sucrose in a solution which remained neutral or, in some cases, became alkaline after contact with the soil. Silicate minerals may be given inverting power by submitting aqueous suspensions to a direct current, and soil acidity is increased by a similar treatment of soils. Contrary to previous conclusions, hydrated oxides of lead, copper, bismuth, aluminium, iron, and zinc were not found to have any inverting power.

The authors consider that the measurement of the power of a soil to catalyse the inversion of cane-sugar is probably the only method by which the acidity bound up with the solid phase of the soil can be measured.   W. G.

Organic Chemistry.

Preparation of Chloroform. SVERRE UTHEIM (Brit. Pat. 116094, 1917).—Acetaldehyde is converted instantaneously and quantitatively into chloroform when a 10% aqueous solution of the aldehyde is introduced into calcium hypochlorite solution at 60° to 80°. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

Alteration of Iodoform, alone or in Solution, in Direct Light. E. COMANDUCCI and G. MEDURI (*Gazzetta*, 1918, **48**, i, 238—247).—The authors have subjected solutions of iodoform in nineteen of the ordinary organic solvents, out of contact with the air, to the action of direct sunlight. The solution (1%) in olive oil remains unchanged after a year. In absence of solvent, iodoform undergoes very little decomposition under the above-named conditions. T. H. P.

Process of Producing Alcohols. E. I. DU PONT DE NEMOURS & Co. (Brit. Pat. 119249).—A suitable halogenated hydrocarbon, for example, a mixture of pentyl and hexyl chlorides, is passed into sodium stearate heated at 200—240° in a distillation vessel provided with a stirrer. The alkyl chloride partly reacts with the sodium stearate to form the stearic ester of an alcohol, and is partly decomposed into olefines. Arrangements are made for separating the olefines from the unchanged alkyl chloride by condensation and returning the latter to the reaction vessel. The stearic ester is cooled to 150° and treated with sufficient sodium hydroxide solution to replace the sodium which has reacted with the chloride. The mixture is again gradually heated to 200—240°, and the alcohol liberated from the ester is distilled off in the presence of water or steam. The sodium stearate is then ready for a fresh treatment, and may be used repeatedly until the accumulation of sodium chloride becomes excessive. J. F. B.

The Preparation of Glycols. H. HIBBERT (*Met. and Chem. Eng.*, 1918, **19**, 571—573).—A mixture of glycols in which ethylene glycol predominates may be prepared by decomposing petroleum vapours in an iron tube heated at about 650°, converting the product into dichloroethane, etc., purifying this compound by distillation, and treating the distillates with alkali carbonates in a closed vessel. The products thus obtained are viscous, hygroscopic liquids capable of replacing glycerol for many industrial purposes. The nitrate derivatives are much more stable at low temperatures than glyceryl trinitrate, which when frozen forms an intermediate crystalline modification capable of changing instantly into a totally different crystalline modification. Explosives pre-

pared from glycol nitrates have valuable properties not possessed by nitroglycerin explosives. [See also *J. Soc. Chem. Ind.*, December.] C. A. M.

Ether-like Compounds. II. Ether Alcohols of the Type R·O·CH₂·C(OH)R₂'. M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1917, [*A*], **10**, No. 17, 1—8; from *Chem. Zentr.*, 1918, i, 1144—1145).—In continuation of previous work (A., 1909, i, 869), the following ether alcohols have been prepared: *α-Methoxy-β-methylpropan-β-ol*, OMe·CH₂·CMe₂·OH, from methyl methoxyacetate and magnesium methyl iodide, b. p. 116·6°, D 0·9021; *α-ethoxy-β-methylpropan-β-ol*, b. p. 129·5°, D 0·8786, in which the hydroxyl group is readily replaced by chlorine, for example, with warm 38% hydrochloric acid, with formation of *β-chloro-α-ethoxy-β-methylpropane*, b. p. 62·5°/10 mm.; *α-propoxy-β-methylpropan-β-ol*, b. p. 149·2—150·2°, D 0·8708; *α-methoxy-β-ethylbutan-β-ol*, from magnesium ethyl iodide and methyl methoxyacetate, b. p. 157·7—158·2°, D 0·9071; *α-ethoxy-β-ethylbutan-β-ol*, b. p. 168·0—168·2°, D 0·8901, from which the highly reactive *β-chloro-α-ethoxy-β-ethylbutane* is obtained by means of hydrochloric acid; *α-propoxy-β-ethylbutan-β-ol*, b. p. 184—185°, D 0·8816; *α-methoxy-β-propylpentan-β-ol*, b. p. 192·1—192·6°, D 0·8896; *α-ethoxy-β-propylpentan-β-ol*, b. p. 202·9—203·1°, D 0·8764; *α-n-propoxy-β-n-propylpentan-β-ol*, b. p. 213·5—214·5°, D 0·8790. H. W.

Process for the Production of Methyl Sulphate. EDMOND JOHNSON BOAKE and THOMAS HAROLD DURRANS (Brit. Pat. 119250).—Methyl alcohol is treated with sulphur dioxide and chlorine, either simultaneously or successively, approximately in the proportions of one molecule of each of the gases to two molecules of the alcohol. A slight excess of sulphur dioxide should be present throughout the operation, and the liquid should be kept cool. Methyl chloride is among the gaseous products of the reaction, and may be collected after washing with an alkaline liquid. The residual liquid may be used directly as a methylating agent, or the methyl sulphate may be isolated by distillation under reduced pressure; the yield of methyl sulphate is more than 50% by weight. J. F. B.

Alkylation of Dialkyl Phosphites. T. MILOBENDZKI and T. KNOLL (*Chemik Polski*, 1917, **15**, 79—88; from *Chem. Zentr.*, 1918, i, 993—994).—The experiments were undertaken with the object of converting phosphorous acid or its hydrogen esters into trialkyl phosphites (compare Arbusov, A., 1907, i, 8, 174, 275).

Triethyl borate does not react with diethyl hydrogen phosphite; with the sodium salt of the latter (obtained from the acid ester and sodium in the presence of ether), small amounts of triethyl phosphite are obtained, which, however, are formed during the action of sodium (or magnesium) on the acid ester. Ethyl sulphate

and triethyl phosphite do not cause the alkylation of diethyl sodium phosphite. The sodium salts of dialkyl phosphites are decomposed by heat, diethyl sodium phosphite at 142—143°. Pure magnesium oxide does not react with dipropyl hydrogen phosphite. The dialkyl phosphites do not react with metallic magnesium when dissolved in ether, benzene, or xylene; on the other hand, dimethyl hydrogen phosphite dissolved in pyridine reacts with magnesium at the ordinary temperature, diethyl hydrogen phosphite after initial heating to 100°, dipropyl hydrogen phosphite with greater difficulty, and dibutyl hydrogen phosphite only when heated. *Magnesium diethyl phosphite* is a powder. When metallic magnesium acts on slightly warmed diethyl hydrogen phosphite, triethyl phosphite is formed in 5% yield. H. W.

Tautomerism of the Dialkyl Phosphites. T. MILOBENDZKI (*Chemik Polski*, 1917, **15**, 89—96; from *Chem. Zentr.*, 1918, i, 994. Compare A., 1912, i, 155).—The author's previous conclusions have been somewhat modified as the result of more recent experiments. From the behaviour of the dialkyl phosphites on neutralisation, etc., the conclusion is drawn that if the esters are derivatives of quinquevalent phosphorus and of the pseudo-acids, $PHO(OR)_2$, the salts of the ester are derivatives of tervalent phosphorus, $P(OR)_2 \cdot OMe$. The tautomerism of these substances depends on this factor. H. W.

The Distillation of some Organic Acids with Water; Measure of the Volatilisation. W. ŒCHSNER DE CONINCK and A. RAYNAUD (*Rev. gén. Chim. pure appl.*, 1915, **18**, 134—135).— A repetition of work previously published (compare A., 1915, i, 645). The figures for acetic and *iso*butyric acids are corrected. W. G.

The Distillation of Mixtures of Water and Formic Acid. Hydrate of Formic Acid. W. ŒCHSNER DE CONINCK (*Rev. gén. Chim. pure appl.*, 1916, **19**, 68. Compare A., 1915, i, 645; preceding abstract).—The composition of successive 5 c.c. portions of distillate of varying mixtures of formic acid and water indicate the existence of Roscoe's hydrate of formic acid, $4H \cdot CO_2H, 3H_2O$, b. p. 107—108°. If such a mixture is rectified several times, it gradually loses formic acid and tends towards the hydrate, $H \cdot CO_2H, H_2O$. W. G.

Stereochemical Studies. III. Iodosuccinic Acids. BROR HOLMBERG (*Arkiv. Kem. Min. Geol.*, 1917, **6**, No. 23, pp. 33; from *Chem. Zentr.*, 1918, i, 1147—1148. Compare A., 1913, i, 824; 1914, i, 139; 1917, i, 115).—The preparation of pure *l*-iodosuccinic acid is described, and its decomposition in alkaline, neutral and acid solution, and racemisation by iodides, have been further investigated.

Experiments on the velocity with which *r*-iodosuccinic acid, in aqueous and hydrochloric acid solution and as acid and normal

sodium salt (with and without addition of sodium iodide), yields acid, lead, in conjunction with preparative experiments, to the following scheme:

$$CO_2H \cdot CHI \cdot CH_2 \cdot CO_2H = HI + CO_2H \cdot CH:CH \cdot CO_2H,$$

$$CO_2H \cdot CHI \cdot CH_2 \cdot CO_2H \rightleftharpoons HI + CO_2H \cdot \overline{CH \cdot CH_2 \cdot CO \cdot O}, \qquad \text{and}$$
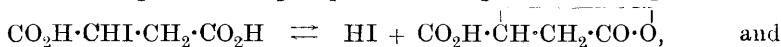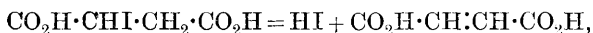
$$CO_2H \cdot \overline{CH \cdot CH_2 \cdot CO \cdot O} + H_2O = CO_2H \cdot CH(OH) \cdot CH_2 \cdot CO_2H.$$ The formation of fumaric acid is greater the more acidic the solution; its production may be due to catalysis by hydrogen ions, but it is probable that the lactonemalic acid, necessary as a step in the formation of malic acid, owes its origin preferentially or almost entirely to the anions of iodosuccinic acid (or to the corresponding salt molecules), and in this case the presence of a strong acid must retard the formation of malic acid.

Kinetic and preparative experiments on the decomposition of iodosuccinic acid by alkali lead to the following scheme:

$$CO_2M \cdot CHI \cdot CH_2 \cdot CO_2M + MOH = CO_2M \cdot CH:CH \cdot CO_2M + MI + H_2O,$$

$$CO_2M \cdot CHI \cdot CH_2 \cdot CO_2M \rightleftharpoons MI + CO_2M \cdot \overline{CH \cdot CH_2 \cdot CO \cdot O}, \qquad \text{and}$$
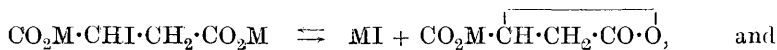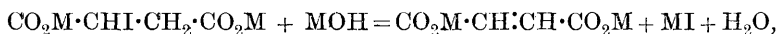
$$CO_2M \cdot \overline{CH \cdot CH_2 \cdot CO \cdot O} + MOH = CO_2M \cdot CH(OH) \cdot CH_2 \cdot CO_2M.$$ Formation of fumaric acid is the main reaction even in strongly alkaline solution. It follows from the equations that, to secure a good yield of malic acid, the solution must be kept as nearly neutral as possible, and, further, that it is advantageous to remove the iodine ions as they are formed. Actually, it has been found possible to obtain *silver lactonemalate*, small prisms, in a pure condition by shaking iodosuccinic acid with an excess of silver oxide, and also to isolate lactonemalic acid in the form of colourless, hygroscopic leaflets or thin plates. When iodosuccinic acid is treated with ammoniacal silver solution, it yields fumaric and β-malamic acids, the latter being formed by the action of ammonia on lactonemalic acid.

l-Iodosuccinic acid, prepared from *d*-lactonemalic acid and potassium iodide, melts at 148—150° to a brownish-black liquid after previously becoming reddish-brown; it has $[\alpha]_D^{19} -89 \cdot 8°$ in ethyl acetate, $[\alpha]_D^{19} -76 \cdot 2°$ in alcohol, $[\alpha]_D^{19} -54 \cdot 9°$ in water, $[\alpha]_D^{19} -56 \cdot 1°$ in $0 \cdot 5N$-sulphuric acid, $[\alpha]_D^{19} -35 \cdot 6°$ as sodium hydrogen salt in water, and $[\alpha]_D^{19} -46 \cdot 5°$ as normal sodium salt in water.

Stereochemical experiments on the decomposition of *l*-iodosuccinic acid have shown that the relationships are exactly similar to those observed with *l*-bromosuccinic acid. *d*-Lactonemalic acid is formed from *l*-iodosuccinic acid in acid, neutral, or alkaline solution in the presence and absence of silver salts; in acid solution, *d*-lactonemalic acid yields mainly *l*-malic acid, whilst in alkaline solution it produces chiefly *d*-malic acid. The latter acid is also obtained when ammonia is employed, but probably results from *d*-β-malamic acid, the primary product of the action of ammonia on *d*-lactonemalic acid.

l-Iodosuccinic acid is far more rapidly racemised by iodine ions than is *l*-bromosuccinic acid by bromine ions. Racemisation is found to follow the simple law $C = 1/0.4343T \cdot \log d_0/dT$, and C is proportional to the concentration of iodine ions in the solution and has the value $1/2.45[T]$ when the solution is about 0.2 molar with respect to *l*-iodosuccinic acid. From this factor and the value of C at different concentrations of sodium and potassium iodide, the electrolytic dissociation constants of the salts is calculated to be 2.5; the conversely calculated velocity constants are in complete agreement with the experimental results. The free acid is racemised about nine times as rapidly as a normal and three times as rapidly as an acid salt. In agreement with this result, the velocity of racemisation is found to be somewhat less when the solution is more dilute with respect to acid. The mechanism of racemisation is the same as in the case of *l*-bromosuccinic acid, namely, the iodine in iodosuccinic acid is replaced by ionised iodine and the substitution is accompanied by a Walden inversion. H. W.

A Direct Rupture of the Benzene Ring without Degradation. II. H. PAULY and G. WILL (*Annalen*, 1918, **416**, 1—20. Compare A., 1914, i, 485).—The authors have already shown that when 3-nitro-*p*-cresol is warmed with concentrated sulphuric acid, hydroxylamine and β-methyl-γ-crotonolactone-γ-acetic acid (I) are formed, and they have suggested that the immediate precursor of the lactonic acid is β-methylmuconic acid (II).

$$\begin{array}{l} \text{CH}{:}\text{CMe} \\ | \qquad\qquad {>}\text{CH}{\cdot}\text{CH}_2{\cdot}\text{CO}_2\text{H} \\ \text{CO}{-}{-}{-}\text{O} \end{array} \qquad \begin{array}{l} \text{CMe}{:}\text{CH}{\cdot}\text{CO}_2\text{H} \\ | \\ \text{CH}{:}\text{CH}{\cdot}\text{CO}_2\text{H} \end{array}$$

(I.)　　　　　　　　　　(II.)
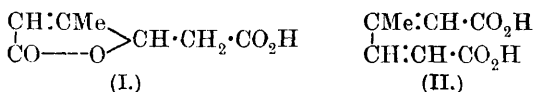
It is now shown that the latter acid can be prepared from the lactone and easily reconverted into it.

The optimum temperature for the above hydrolytic rupture of 3-nitro-*p*-cresol is 111—113°. The nitrogenous acid by-product (*ibid.*) reacts very slowly with methyl-alcoholic hydrogen chloride compared with the lactonic acid, and a separation of the acids is best effected by taking advantage of this fact. The methyl ester of the lactonic acid (now called *isoprenelactonic* or β-*methylmucolactonic* acid) has b. p. 310°/atm., and is hydrolysed by treatment with sodium methoxide solution to *methyl hydrogen β-methylmuconate* (*isoprenedicarboxylate*), which crystallises in needles, m. p. 125°. This is converted into the free *acid* (II), m. p. 171°, by hydrolysis with sodium hydroxide, and into the *dimethyl* ester, long, glistening needles, b. p. 142—143°/16 mm., m. p. 38.5°, by means of methyl sulphate. The acid resembles muconic acid in forming very sparingly soluble barium, silver, and lead salts, and the methyl ester, like isoprene, changes in the course of time into a pale, elastic polymeride. The corresponding *diamide* has m. p. 213—214°, and becomes deep bluish-green when kept molten for a few minutes; *methyl β-methylmuconamate* forms

stout prisms, m. p. 161—162°, and the vapours obtained by heating it with zinc dust give the pyrrole reactions.

The reconversion of the dicarboxylic acid into the lactonic acid can be effected by means of warm sulphuric acid, glacial acetic acid solutions of hydrogen chloride or bromide, or by melting. Similarly, the above methyl hydrogen ester yields the methyl ester of the lactonic acid when heated at 210°.

The dicarboxylic acid is most readily reduced by sodium amalgam, the product being *β-methyl-Δβ-butene-αδ-dicarboxylic acid*, $CO_2H \cdot CH_2 \cdot CMe\!:\!CH \cdot CH_2 \cdot CO_2H$. This was prepared previously from the lactonic acid and designated β-methyldihydromuconic acid, but the position of the ethylene linking remained to be proved. The acid, m. p. 140—141°, couples with diazonium salts, which, from analogy to glutaconic acid, shows that the double bond is in the middle of the chain. The *methyl* ester is a limpid liquid with the odour of melons, b. p. 245°/753 mm., D_0^{0} 1·0824, and yields methyl acetoacetate when its ozonide is boiled with water, this fact also attesting to the position of the ethylene linking.

The free isoprenedicarboxylic acid reacts vigorously with bromine, hydrogen bromide being evolved, but its methyl ester absorbs four atomic proportions of bromine fairly readily. The above butene-dicarboxylic acid also absorbs bromine at 40—50°, giving *βγ-dibromo-β-methyladipic acid*, $CO_2H \cdot CH_2 \cdot CMeBr \cdot CHBr \cdot CH_2 \cdot CO_2H$, m. p. 166°, which is decomposed by boiling alcoholic potassium hydroxide, the products including isoprene and the above isoprene-dicarboxylic acid.　　　　　　　　　　　　　　　　J. C. W.

Synthesis of Linamarin. EMIL FISCHER and GERDA ANGER (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 203—212; from *Chem. Zentr.*, 1918, i, 1163—1164).—The synthetical methods used by Fischer and Bergmann (A., 1917, i, 657) for the preparation of mandelonitrileglucoside and sambunigrin can be extended to aliphatic hydroxy-acids; the present communication describes the synthesis of linamarin, the glucoside of acetonecyanohydrin,

$$C_6H_{11}O_5 \cdot O \cdot CMe_2 \cdot CN,$$
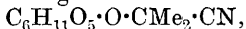
which appears to be a β-glucoside.

A mixture of acetobromoglucose and ethyl α-hydroxy*iso*butyrate is shaken with silver oxide, whereby *ethyl tetra-acetylglucosido-α-hydroxybutyrate*, $(OAc)_4C_6H_7O_5 \cdot O \cdot CMe_2 \cdot CO_2Et$, m. p. 114—115° (corr.), $[\alpha]_D^{20}$ −11·17° in acetone, is produced. This is converted by ammonia into *α-hydroxybutyramideglucoside*,

$$C_6H_{11}O_5 \cdot O \cdot CMe_2 \cdot CO \cdot NH_2,$$

needles, m. p. 166—167°, $[\alpha]_D^{18}$ −24·53° in water, which is extremely slowly hydrolysed by emulsin; in the absence of seeding material, the product can only be induced to crystallise with great difficulty when prepared in this manner, and it is preferable to obtain it from the *tetra-acetyl* derivative. The latter is obtained by acetylating the crude substance obtained in the reaction just described with acetic anhydride in the presence of pyridine; it melts at

153—154° (corr.) and has $[\alpha]_D^{20}$ −21·07° in aqueous solution; it is transformed into the free amide by treatment of its methyl-alcoholic solution with ammonia. *Tetra-acetyl-linamarin*,

$$(OAc)_4C_6H_7O_5 \cdot O \cdot CMe_2 \cdot CN,$$
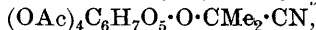
needles, m. p. 140—141° (corr.), $[\alpha]_D^{14}$ −10·81°, is prepared by the action of phosphoryl chloride on tetra-acetyl-α-hydroxybutyramide-glucoside at 65—68°, or by the acetylation of linamarin by acetic anhydride in the presence of pyridine. Linamarin itself is prepared by shaking an ice-cold methyl-alcoholic solution of the tetra-acetate with methyl-alcoholic ammonia; it crystallises in needles, m. p. 142—143° (corr.), $[\alpha]_D^{19}$ −29·10°. Reduction does not occur when it is boiled for a short time with Fehling's solution.

<div align="right">H. W.</div>

Conversion of *l*-Glucosan into Dextrin. AMÉ PICTET (*Helv. Chim. Acta*, 1918, **1**, 226—230).—When kept at 240° for thirty to sixty minutes, or, better, at 180° for a few minutes in the presence of a little platinum-black as catalyst, *l*-glucosan undergoes polymerisation and is transformed into a white, amorphous *substance*, $(C_6H_{10}O_5)_4$, $[\alpha]_D$ varying from +111·9° to +106·5° in different preparations, which exhibits the characteristic properties of a dextrin and yields dextrose when warmed with dilute sulphuric acid (compare Pictet and Sarasin, this vol., i, 59; *Helv. Chim. Acta*, 1918, **1**, 87).

<div align="right">C. S.</div>

Preparation of Methylamine. HILTON IRA JONES and RUTH WHEATLEY (*J. Amer. Chem. Soc.*, 1918, **40**, 1411—1415).—The results recently published by Werner (T., 1917, **111**, 844) have led the authors to describe certain experiments made with the object of studying the effect of reduced pressure on those organic reactions in which a gas is evolved.

Mixtures of ammonium chloride and formaldehyde were (1) slowly distilled at the ordinary pressure, (2) slowly distilled in a vacuum, (3) heated under reflux during eight hours and then distilled at the ordinary pressure, and (4) heated under reflux during four and a-half hours and then distilled in a vacuum.

The authors are led to the following conclusions: The vacuum heating under reflux and distillation decreases the amount of ammonium chloride left unused, lowers the temperature, and therefore decreases the yield of dimethylamine and more highly methylated substances, which agrees with Werner's theory, and it increases the acidity of the distillate, the loss of carbon dioxide, and the weight of methylamine produced.

The vacuum distillation, merely by removing the volatile products as well as the carbon dioxide, causes a marked increase in the weight of the distillate and the amount of ammonium chloride remaining unchanged; it causes the formation of the lowest percentage of dimethylamine, but also lowers markedly the amount of methylamine formed, and it brings about a higher percentage of esterification and gives a distillate of the highest rotatory power.

The long heating at ordinary pressure and relatively high

temperature gives the smallest percentage of distillate, the highest percentage of non-distillate residue, the highest percentage of esterification, uses up a large amount of ammonium chloride, and gives the highest degree of methylation, which means the highest percentage of dimethyl and other more highly methylated derivatives, most of which will not crystallise.

The theory advanced by Werner is correct and explains all the observed facts.

The four types of reaction agree with the principles of a larger theory which applies to all organic reactions of this type in which a gas is evolved; this is being worked out in other cases.

Methylamine is best prepared by heating under reflux in a vacuum. H. W.

Preparation of Compounds of Carbamide and a Calcium Salt. KNOLL & Co. (D.R.-P. 306804; from *Chem. Zentr.*, 1918, ii, 420).—The *compound*, $CaCl_2,4CO(NH_2)_2$, white powder, stable in air and very readily soluble in water, m. p. 158—160°, is obtained by evaporating an aqueous solution of the components in the required proportion to dryness, or of an alcoholic solution to crystallisation; it is useful for subcutaneous injection in hay fever and asthma, since it does not give rise to pain as with calcium chloride alone. The compounds of calcium chloride with one, two, or three molecules of carbamide are hygroscopic, whilst those with more than four molecules have a too low content of calcium chloride for pharmaceutical purposes. H. W.

Constitution of Carbamides. VII. The Mechanism of the Synthesis of Urea from the Interaction of Carbonyl Chloride and Ammonia. VIII. Formation of Urea and Biuret from Oxamide. EMIL ALPHONSE WERNER (T., 1918, 113, 694—701).—VII. The production of urea by the action of carbonyl chloride on ammonia is usually regarded as evidence of the "carbamide" structure for urea. It is now shown, however, that considerable quantities of biuret, ammelide, and cyanuric acid, and traces of cyamelide, are formed as well, biuret being observed for the first time. Taking these by-products into consideration, the "synthesis" really affords evidence in support of the view that urea is the product of the union of ammonia and cyanic acid in its keto-form. The mechanism of the reactions is expressed as follows:

$$COCl_2 + 2NH_3 \longrightarrow NH_2 \cdot COCl \longrightarrow$$
$$+ N\overset{..}{H}_4Cl$$

$$HCl + \quad \begin{matrix} HO \cdot CN & \longrightarrow & \text{Cyamelide} \\ \downarrow \uparrow & & \text{by} \\ & & \text{polymerisation} \\ HN \colon CO & \longrightarrow & \text{Cyanuric acid} \end{matrix}$$
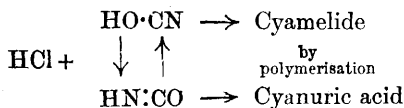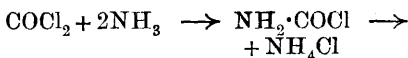
Urea then arises from the union of ammonia and $HN\colon CO$, biuret from the interaction of urea and cyanic acid, and ammelide from the biuret and cyanic acid.

VIII. [With George Kingsford Carpenter.]—When oxamide is heated to a temperature sufficient to effect complete volatilisation, ammonium cyanate, urea, and biuret are found in the sublimate, and ammonia, water, carbon monoxide, and hydrogen cyanide are evolved. The decomposition is represented thus:

(a) $\begin{array}{c} CO \cdot NH_2 \\ | \\ CO \cdot NH_2 \\ \downarrow\uparrow \end{array}$ $\rightarrow$ $NH_3 + \overset{CO}{\underset{CO}{>}}NH \rightarrow CO + \begin{array}{c} \rightarrow HO \cdot CN = NH_4 \cdot O \cdot CN \\ \downarrow\uparrow \\ \rightarrow HN{:}CO = CON_2H_4 \end{array}$

(b) $\begin{array}{c} HO \cdot C{:}NH \\ | \\ HO \cdot C{:}NH \end{array}$ $\rightarrow$ $H_2O + O{<}\overset{C{:}NH}{\underset{C{:}NH}{}}$ $\rightarrow HN{:}CO + HCN$.
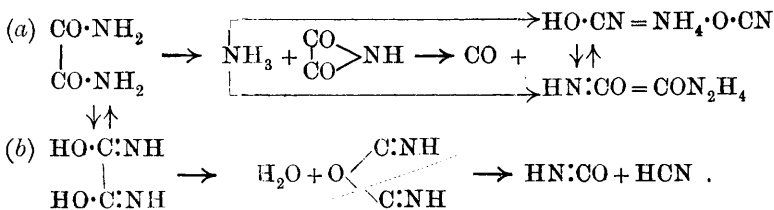
J. C. W.

Stereochemical Studies. III. Xantho- and Thiol-β-succinnamic Acids. B. Holmberg and K. J. Lenander (*Arkiv Kem. Min. Geol.*, 1917, **6**, No. 17, pp. 26; from *Chem. Zentr.*, 1918, i, 1145—1146. Compare A., 1917, i, 115).—Previous investigations (A., 1914, i, 140) have shown that, according to the experimental conditions, a lævo- or dextro-rotatory xanthosuccinic acid can be obtained by the action of potassium xanthate on salts of l-bromosuccinic acid, whilst salts of l-β-bromosuccinamic acid only yield a dextrorotatory xanthosuccinamic acid of constant specific rotation when treated with xanthates. It further appears that xanthosuccinic acid is formed from l-bromosuccinic acid by direct substitution (d-acid) and by addition of xanthate to the primarily formed d-lactonemalic acid (l-acid), and that change of configuration occurs with direct substitution. The reaction between xanthates and salts of l-bromosuccinamic acid can only be a case of direct substitution, and opposite configurations must therefore be ascribed to l-bromosuccinamic acid and d-xanthosuccinamic acid. To test this point, the reaction between potassium xanthate and salts of l-bromosuccinamic acid has been thoroughly investigated, and the relationships between the active xantho- and thiolsuccinic acids and the corresponding active β-substituted succinamic acids have been established.

Kinetic investigations of the action of potassium xanthate on the salts of l-bromosuccinamic acid lead to velocity constants of the second order which diminish slightly as the action proceeds, and are rather greater with barium and strontium than with sodium and potassium salts. As the reaction proceeds slowly, so that the bromosuccinamic acid may be, in part, decomposed by the water (thus explaining the slight decrease in the velocity constants), it appears that the xanthosuccinamic acid is entirely formed in accordance with the scheme:

$CO_2M \cdot CHBr \cdot CH_2 \cdot CO \cdot NH_2 + KS \cdot CS \cdot OEt =$

$KBr + CO_2M \cdot CH(S \cdot CS \cdot OEt) \cdot CH_2 \cdot CO \cdot NH_2$,
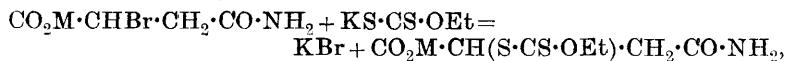
and that the reaction is only slightly accelerated by metallic ions. d-Thiolsuccinic acid is formed from d-thiolsuccinamic acid

c c*

by hydrolysis in acid or alkaline solution. The mutual relationships of the individual acids are shown in the following scheme, in which the dotted arrows denote reactions which occur without affecting the asymmetric carbon atom, whilst straight and zig-zag arrows show actions taking place without and with change of configuration respectively:

l-Bromosuccinamic acid $\xrightarrow{\text{NO+Br+H}_2\text{O}}$ l-bromosuccinic acid

Potassium xanthate   *Potassium xanthate*   *through lactoenamic acid*   *Potassium xanthate*

d Xanthosuccinamic acid $\xrightarrow{\text{H}_2\text{O}}$ d-xanthosuccinic acid l-xanthosuccinic acid

NH$_3$ *NH$_3$*   *NH$_3$*

d-Thiolsuccinamic acid $\xrightarrow{\text{H}_2\text{O}}$ d-thiolsuccinic acid l-thiolsuccinic acid
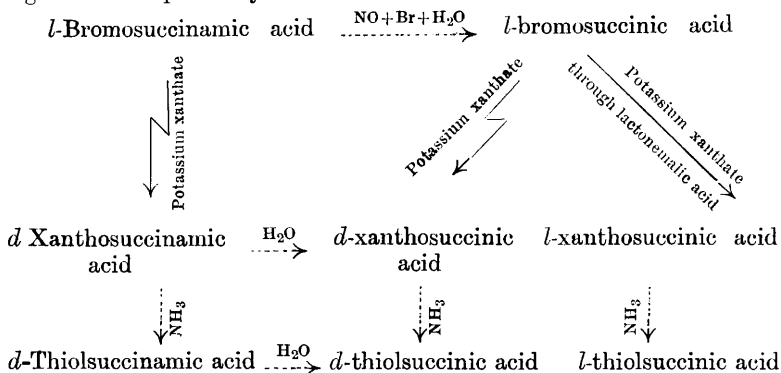
r-β-Xanthosuccinamic acid forms silky platelets, m. p. 125—126° (decomp.). The corresponding d-acid is prepared by the action of potassium xanthate on potassium, sodium, or strontium l-bromosuccinamates; after exhaustive purification, it has m. p. 134—135° (decomp.), $[\alpha]_D^{18}$ +53·1° ($c=2·769$) and $[\alpha]_D^{18}$ +55·5° ($c=6·597$) in acetone, $[\alpha]_D^{17}$ +66·0° in ethyl acetate; it is slowly racemised and slightly decomposed when its solution in ethyl acetate is heated. l-β-$Xanthosuccinamic$ $acid$ is obtained by resolution of the inactive acid with d-phenethylamine; it has m. p. 134—135° (decomp.), $[\alpha]_D^{19}$ −53·4° ($c=4·055$) in acetone.

r-β-$Thiolsuccinamic$ $acid$, prepared by the action of ammonia on r-xanthosuccinamic acid or by mixture of equal weights of the components, crystallises in plates, m. p. 103—104° (decomp.). The corresponding d-$acid$, small, colourless prisms, m. p. 125—126° (decomp.), has $[\alpha]_D^{18}$ +82·5° in acetone, $[\alpha]_D^{18}$ +58·7° in water, whilst the $sodium$ salt has $[\alpha]_D^{18}$ +36·8° in water; the $ammonium$ salt forms colourless plates or thin prisms, $[\alpha]_D^{19}$ +33·6° in water. l-β-$Thiolsuccinamic$ $acid$ has m. p. 125—126° (decomp.), $[\alpha]_D^{18}$ −82·9° in acetone.   H. W.

Epimeric Hexosamic Acids. P. A. Levene (*J. Biol. Chem.*, 1918, **36**, 73—87. Compare Levene and La Forge, A., 1915, i, 782, 944).—The author attempts to determine the position of the amino-group in various amino-sugars by comparing the properties of pairs of epimeric hexonic acids with corresponding pairs of hexosamic acids, especially with regard to the equilibrium of the two epimerides formed on the synthesis of the hexoic acids from the corresponding pentoses and the direction of the rotation of the α-carbon atom in corresponding pairs of epimerides. Three pairs

of epimeric α-hexosamic acids have been prepared and examined; two arabinohexosamic acids, two lyxohexosamic acids, and two xylohexosamic acids. Of the first pair, one is prepared by the oxidation of chitosamine (glucosamine) and the other by the action of pyridine on chitosamic (glucosamic) acid. *Epichitosamolactone hydrochloride*, $C_6H_{12}O_5NCl$, is prepared by treating the raw product, obtained by the action of pyridine on chitosamic acid, with alcohol and benzaldehyde, and then with gaseous hydrogen chloride. The addition of the benzaldehyde has for its purpose the conversion of the chitosamic acid into the benzylidene compound of its ethyl ester, which remains in solution. The lactone is precipitated by ether and recrystallised from methyl alcohol. It crystallises in prismatic needles, m. p. 203° (decomp.), $[\alpha]_D^{20} + 45°$. On dissolving in water rendered alkaline with barium hydroxide, the lactone is converted into the free *epichitosamic acid*, $C_6H_{13}O_6N$, colourless, prismatic needles, m. p. 198° (decomp.), $[\alpha]_D^{20}$ initial $+10°$, equilibrium $+39°$. The rotation of chitosamic acid being $-15·02°$, that of the α-carbon atom is $\{10·0-(-15·02)\}/2 = 12·51°$.

A mixture of chondrosamic and epichondrosamic acids is obtained by the action of hydrocyanic acid on lyxose in the presence of ammonia. The reaction is very capricious, the result obtained depending on the temperature and the duration of the reaction, the optimum values for which have to be determined empirically for each sugar. When successful, the yield amounts to 50% of the theoretical quantity, but often, with the best care, it falls to 25%, or even less. The mixture of epimerides can be separated by fractional crystallisation from dilute methyl alcohol; d-*chondrosamic acid*, $C_6H_{13}O_6N$, has m. p. 206° (decomp.) and $[\alpha]_D^{20} - 17·0°$, whilst d-*epichondrosamic acid* has $[\alpha]_D^{20} + 8·0°$, the numerical value of the α-carbon atom being again $12·5°$.

d-Xylohexosamic acid, as prepared by Levene and La Forge (*loc. cit.*), was not pure, but consisted of a mixture of the two epimerides. It has now been prepared synthetically from xylose by the action of hydrocyanic acid, the product being fractionated in a similar manner to that indicated in the case of the chondrosamic acids. d-d-*Xylohexosamic acid*, $C_6H_{13}O_5N$, has m. p. 224° (decomp.) and $[\alpha]_D^{20} + 14°$, whilst d-l-*xylohexosamic acid* has m. p. 200° (decomp.) and $[\alpha]_D^{20} - 11·0°$, the value for the rotation of the α-carbon atom being $12·5°$, as before. Both epimerides were converted into lactones. d-d-*Xylohexosamolactone hydrochloride*, $C_6H_{12}O_5NCl$, has m. p. 205° (decomp.), and on treatment with barium hydroxide is reconverted into the parent acid. The other lactone was obtained in the form of its benzaldehyde derivative by treating d-l-hexosamic acid in alcoholic solution with benzaldehyde and passing in hydrogen chloride. Crystallisation occurs spontaneously. After recrystallisation, *benzylidene*-d-l-*xylohexosamic-lactone hydrochloride*. $C_{13}H_{15}O_5N.HCl$, melts at 206° (decomp.) and has a rotation of $[\alpha]_D^{20} - 60·5°$. It is readily transformed into the parent acid by means of barium hydroxide.

After comparison of the rotations of these hexosamic acids with the corresponding hexonic acids, the authors suggest probable configurations for these three pairs of epimeric acids.

<div align="right">H. W. B.</div>

Action of Nitrous Acid on Epimeric Hexosamic Acids. P. A. LEVENE (*J. Biol. Chem.*, 1918, **36**, 89—94. Compare preceding abstract).—Levene and La Forge (A., 1915, i, 786) have shown that the replacement of the amino-group by hydroxyl in amino-sugars and their derivatives probably takes place with the intermediate formation of a diazo-compound. Accepting for the structure of the diazo-compound the expression

$$OH \cdot CH_2 \cdot [CH \cdot OH]_3 \cdot C \cdot CO_2H$$
$$\overset{\diagup \diagdown}{N \! = \! N}$$
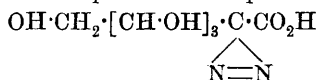
it appears that each of a pair of epimerides should give one and the same diazo-compound, and hence one and the same deaminised acid. However, by the action of nitrous acid on the three pairs of epimerides described in the preceding abstract, six different acids are produced. The deaminisation is brought about in each case by dissolving the acid in dilute hydrochloric acid and treating with silver nitrite. The products from the different amino-acids are then treated in various ways. Chitosamic and epichitosamic acids after deamination are reduced, yielding *d*-anhydrogulonic and *d*-anhydromannonic acids respectively; chondrosamic and epichondrosamic acids, after deamination and oxidation, give *d*-anhydromucic and *d*-anhydrotalomucic acids, whilst *d*-*d*-xylohexosamic and *d*-*l*-xylohexosamic acids on similar treatment yield *d*-anhydroidosaccharic and *l*-anhydrosaccharic acids respectively. It is further noted that whereas *d*-xylohexosamic acid and its lactone give *d*-anhydroidosaccharic and *l*-anhydrosaccharic acids respectively, epichitosamic acid and its lactone form the same *d*-anhydromannonic acid. Thus, whilst in the first instance a Walden inversion takes place, in either the acid or the lactone, in the second the inversion occurs in neither or in both. H. W. B.

Direct Transformation of Acid Chlorides into Nitriles by Catalysts. ALPH. MAILHE (*Bull. Soc. chim.*, 1918, [iv], **23,** 380—381).—Acid chlorides may be converted directly into the corresponding nitriles by passing their vapours, along with ammonia, over aluminium oxide at 490—500°. Excellent yields were obtained from benzoyl, *iso*valeryl, *iso*butyryl, and propionyl chlorides. W. G.

[Reactions of] Cyanogen Products. V. MACRI (*Boll. chim. farm.*, 1918, **57**, 261—265).—The author has purified the crude carbonylferrocyanide obtained from the wash-waters of the Laming mixture, and has subjected the pure product, and also alkali cyanide, thiocyanate, and ferrocyanide, to the action of a number

of reagents; the results are tabulated. The carbonylferrocyanide is a highly stable compound. T. H. P.

Chromithiocyanic Acid and Chromithiocyanates. Gino Scagliarini (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 442—445).— In order to obtain salts of bivalent metals with chromithiocyanic acid, the author has made use of hexamethylenetetramine, which combines with the hydrates of the salts in solution to form stable and insoluble, wine-red double compounds, these being isomorphous and of the general formula $M''_3[Cr(SCN)_6],10H_2O,3C_6H_{12}N_4$. A concentrated solution of the hexamethylenetetramine was added to a solution containing either ammonium chromithiocyanate and a soluble salt of the metal in question, or barium chromithiocyanate and the sulphate of the metal. In this way, the compounds of hexamethylenetetramine with the chromithiocyanates of manganese, cobalt, nickel, magnesium, calcium, zinc, cadmium, and strontium were prepared, the first five being analysed.

Chromithiocyanic acid, $H_3Cr(SCN)_6$, may be prepared by treating a concentrated solution of the ammonium or barium salt (1 mol.) with 10% sulphuric acid (3 mols.) solution in the cold. The liquid is extracted repeatedly with ether until the solvent is no longer coloured red, the ethereal solution being washed with water until all sulphuric acid is removed, and dried with anhydrous sodium sulphate. After evaporation of the ether, the chromithiocyanic acid remains as a bright red oil which does not solidify in a mixture of ice and salt, and does not decompose below about 40°, but at higher temperatures emits hydrocyanic acid and vapours of alliaceous odour. It is a moderately energetic acid almost comparable with the mineral acids; thus, a solution of normal concentration attacks metals, for instance, zinc turnings, in the cold with evolution of hydrogen. The electrical conductivities of its solutions at 25° are a little greater than those of equivalent solutions of phosphoric acid. T. H. P.

Preparation of Ethanoltrialkylarsonium Hydroxides and their Salts. Chemische Werke Grenzach (D.R.-P., 305772; from *Chem. Zentr.*, 1918, ii, 83).—Arsonium compounds of the choline type are prepared by the action of glycol halogenhydrins on trialkylarsines; they possess valuable therapeutic properties.

Trimethylethanolarsonium hydrochloride, $C_5H_{14}OAsCl$, very hygroscopic, prismatic crystals, m. p. 218—220°, is produced from glycol chlorohydrin and trimethylarsine at 120—125°; the free *base* forms a viscous mass which slowly crystallises and reacts strongly alkaline. Hydrogen sulphide does not give a precipitate with the aqueous solution of the hydrochloride; with mercuric chloride, a crystalline double salt is formed. Mayer's reagent gives a faint white, potassium iodide and iodine a dirty brown precipitate. Phosphotungstic acid gives a copious white precipitate. The *hydriodide* forms long, hygroscopic needles; the *sulphate*, m. p. 240°, is hygroscopic. The *di-iodosalicylate*, m. p. 140°, is stable in the

air. The *picrate, gold* and *platinum* salts, and the *picrolonate* are also described. *Trimethylethanolarsonium hydrobromide* forms thick, hygroscopic prisms, m. p. 219°. *Triethylethanolarsonium hydrochloride* consists of slender, very hygroscopic needles; the free *base* forms a viscous mass. The *di-iodosalicylate*, m. p. 118°, is stable in the air, as is also the *triborate*. The *picrate* has m. p. 152°.   H. W.

Unsaturation and Molecular Compound Formation. O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1561—1573).—Freezing-point determinations of mixtures of benzene, toluene, ethylbenzene, mesitylene, and acetylene, respectively, with hydrogen bromide have been made, and the freezing-point curves constructed with the object of ascertaining the influence of structure on the formation of additive compounds. It is shown that acetylene and benzene do not form molecular compounds with hydrogen bromide at low temperatures. The existence of the compound, $2C_6H_5Me,HBr$, m. p. $-86.5°$, has been verified, and the existence of compounds, C_6H_5Et,HBr, m. p. $-105.5°$, $2C_6H_5Et,HBr$, m. p. $-103.8°$, and $C_6H_3Me_3,HBr$, m. p. $-61°$, demonstrated.   J. F. S.

Intramolecular Migrations of the Phenyl Group. P. J. MONTAGNE (*Chem. Weekblad*, 1918, **15**, 1195—1204).—A lecture delivered before the Chemical Society of Leyden.   A. J. W.

The Freezing-point Curve of Mixtures of Toluene-*o*- and -*p*-sulphonamides. Composition of Mixtures of Toluene-*o*- and -*p*-sulphonic Acids. PHYLLIS VIOLET MCKIE (T., 1918, **113**, 799—803).—The freezing-point curve of mixtures of toluene-*o*- and -*p*-sulphonamides is a simple one, giving a well-defined eutectic, m. p. 110·25°, containing 61·25% of the *p*-sulphonamide. The *o*-amide has m. p. 156·3° and the *p*-amide m. p. 137·45°. This curve can be used to determine the composition of mixtures of the respective acids by converting them into the amides through the chlorides, and determining the melting point of the resulting mixture of amides.   T. S. P.

Preparation of Hydrogenated Compounds. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 306724; additional to D.R.-P. 305347; from *Chem. Zentr.*, 1918, ii, 420).—Other aromatic isocyclic and heterocyclic compounds, in addition to bases, can be reduced with alkali or alkaline earth metals and alcohol in the presence of an indifferent solvent. The process is easily regulated and can be stopped at any point by withholding further addition of alcohol. Thus, tetrahydronaphthalene is obtained from naphthalene, sodium, and alcohol in the presence of solvent naphtha at 140—145°, and *tetrahydrodiphenyl*, b. p. 247—249°, 115—118°/10—12 mm., from diphenyl, sodium, alcohol, and solvent naphtha at 140—150°. Acenaphthene yields tetra-hydroacenaphthene   H. W.

Preparation of Certain Organic Stanno- and Stanni-chlorides. JOHN GERALD FREDERICK DRUCE (T., 1918, **113**, 715—718).—Diethylamine stannochloride, the stanno- and stanni-chlorides of *o*-toluidine, methylaniline, *m*- and *p*-phenylenediamine and benzylamine, and *p*-methylbenzylamine stannochloride have been prepared from hydrochloric acid solutions of the component haloids. J. C. W.

Preparation and Properties of Aniline Stannichloride. J. G. F. DRUCE (*Chem. News*, 1918, **117**, 346—348).—A crystalline hydrate of aniline stannichloride, $(NH_2Ph)_2,H_2SnCl_6,3H_2O$, is obtained in pale pink tablets by crystallising a mixture of two mole-cules of aniline and one molecule of stannic chloride from hydro-chloric acid. This compound loses water on heating, with the formation of an amorphous residue which melts at 292° to a dark brown liquid. The anhydrous compound is best prepared by add-ing 80 c.c. of concentrated hydrochloric acid to a mixture of 15 grams of tin and 10 grams of nitrobenzene, heating until the nitro-compound has been reduced, and then cooling. The cold, solid mass is dissolved in 200 c.c. of warm diluted hydrochloric acid, and 18 grams of aniline added. On cooling, an almost quantitative yield of the anhydrous aniline stannichloride is obtained. A number of other methods of preparation are given. It is a colourless, crystalline compound, m. p. 293° (slight decomp.). It dissolves in water to the extent of 28 grams in 100 c.c. at 16°. On keeping, it darkens. This compound may be used in the preparation of quinoline instead of a mixture of aniline and nitrobenzene. J. F. S.

Influence of Temperature on the Decomposition of Sodium Phenoxide and Tolyloxides by Carbon Dioxide. G. J. DENBIGH (*J. Soc. Chem. Ind.*, 1918, **37**, 306—307T).—The liberation of phenol and the cresols from solution in sodium hydr-oxide by means of carbon dioxide has been studied under various conditions of temperature. The author is led to the conclusion that all three cresols are more easily liberated than phenol, and, further, that they only differ slightly among themselves in this respect, *m*-cresol being most readily and *o*-cresol least easily set free. In the case of both phenol and cresols, the decomposition is more com-plete when warm, and the rate increases more rapidly with all the cresols than with phenol.

Attempts have been made to separate phenol from cresol by fractional decomposition; the work is being continued in this direction. H. W.

Tartaric Amides and Imides. II. LUIGI CASALE (*Gazzetta*, 1918, **48**, i. 114—120).—p-*Aminophenol hydrogen* d-*tartrate*, $CO_2H \cdot [CH \cdot OH]_2 \cdot CO_2H, NH_2 \cdot C_6H_4 \cdot OH$, forms colourless scales, m. p. 232° (corr.).

p-*Hydroxyphenyltartrimide*, $\begin{matrix} CH(OH) \cdot CO \\ CH(OH) \cdot CO \end{matrix}\Big> N \cdot C_6H_4 \cdot OH$, obtained

by heating the above salt in a vacuum at about 200°, forms long, silky, colourless needles, m. p. 299° (corr.; decomp.), $[\alpha]_D^{20} +119·64°$, $[\alpha]_D^{15} +120·7°$; its solubility in methyl alcohol at 13° is 2·913%.

d-*Hydroxyphenyltartramide*,

$$OH·C_6H_4·NH·CO·CH(OH)·CH(OH)·CO·NH_2,$$
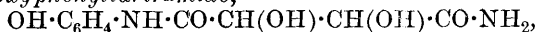
forms white needles, m. p. 227° (corr.), $[\alpha]_D^{15} +154°$; its solubility in methyl alcohol at 15° is 1·58%.

d-*Phenylhydroxyphenyltartramide*,

$$OH·C_6H_4·NH·CO·CH(OH)·CH(OH)·CO·NHPh,$$
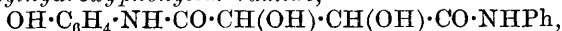
prepared by heating the preceding compound in presence of aniline, forms silky, white needles, m. p. 253° (corr.); its solubility in methyl alcohol at 15° is 1·582%.

p-*Hydroxyphenyltartramic acid*,

$$OH·C_6H_4·NH·CO·CH(OH)·CH(OH)·CO_2H,$$
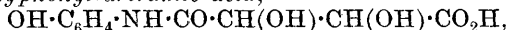
forms white plates, m. p. 218° (corr.), $[\alpha]_D^{14} +108·3°$, and, when heated slowly, is transformed into the imide without melting; its solubility in water at 14° is 4·215%. The *methyl*, m. p. 206° (corr.; decomp.), $[\alpha]_D^{15} +109·5°$, *ethyl*, m. p. 118° (corr.), $[\alpha]_D^{15} +106·1°$, and *propyl* esters, m. p. 133° (corr.), $[\alpha]_D^{15} +103·8°$, were prepared.

T. H. P.

Benzoylation of some Hydroxyl or Amino–Aromatic Compounds. FRÉDÉRIC REVERDIN (*Helv. Chim. Acta*, 1918, **1**, 205—209).—A mixture of the substance and benzoyl chloride is treated with two or three drops of concentrated sulphuric acid, and, if necessary, warmed for a short time on the water-bath. The method succeeds in benzoylating substances, which are unaffected by the usual methods of benzoylation. Thus, 2 : 3 : 5-trinitro-*p*-anisidine yields a *benzoyl* derivative, colourless needles, m. p. 205°, resorcinol yields a mixture of the mono- and di-benzoates, alizarin yields the *dibenzoate*, $C_{14}H_6O_2(OBz)_2$, yellow needles, m. p. 210—211°, 2 : 4-dinitroaniline yields 2 : 4-dinitrobenzanilide, m. p. 201—202°, 1-aminoanthraquinone yields the benzoyl derivative, m. p. 246°, and 2-aminoanthraquinone yields a *benzoyl* derivative, yellow prisms, m. p. 227°, sintering at 195°.

C. S.

Preparation of Glycollyl-*p*-aminophenyl Ethers. FARBWERKE vorm. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 306938; from *Chem. Zentr.*, 1918, ii, 420—421).—Glycollyl-*p*-aminophenyl ether is obtained in excellent yield and in a high degree of purity by heating *p*-aminophenyl ether with the glycollic anhydrides; the latter are considered to comprise glycollide, m. p. 86°, polyglycollide, m. p. 223°, and the product formed when glycollic acid is heated at about 200—250°, which consists of a crystalline powder insoluble in water, by which it is slowly converted into glycollic acid. Esters of glycollic acid can be used in place of the anhydrides. *Glycollyl-p-phenetidine* forms colourless crystals, m. p. 153°; *glycollyl-p-anisidine* has m. p. 101°.

H. W.

The Bromination of some Derivatives of Veratrole.

JOHN LIONEL SIMONSEN and MADYAR GOPALA RAU (T., 1918, 113, 782—790. Compare T., 1917, 111, 69, 220; this vol., i, 22).— The action of bromine on the two isomeric acetylaminoveratroles and the three acetylaminoveratric acids has been investigated. The bromine always entered the nucleus in the *para*-position with respect to the acetylamino-group, except in the case of 6-acetylaminoveratric acid, when, this position being already occupied, the carboxyl group was eliminated with the formation of 5-bromo-4-acetylaminoveratrole. Only in one case was the formation of an isomeride detected, namely, when 3-acetylaminoveratrole was brominated under special conditions; this isomeride could not be definitely orientated.

In view of the fact that the formation of the bromoamide always preceded substitution in the nucleus, which was therefore indirect, these experiments cannot claim to throw any light on the mechanism of nitration of this type of substance.

For experimental details, the original paper must be consulted.
H. W.

Sulphur Aryl Chlorides. IV. 4-Chloro-2-nitrochlorothiolbenzene (*p*-Chloro-*o*-nitrophenyl Sulphur Chloride). Conversion into Thiazine Derivatives.

TH. ZINCKE and JOHANNA BAEUMER (*Annalen*, 1918, 416, 86—112. Compare this vol., i, 385).—2:5-Dichloronitrobenzene is converted by Wohlfahrt's method (A., 1903, i, 203) into 4:4′-*dichloro-2:2′-dinitro-diphenyl disulphide*, which crystallises in glistening, yellow leaflets, m. p. 212°, and is transformed by treatment with chlorine in chloroform into 4-*chloro-2-nitrochlorothiolbenzene*,

$$NO_2 \cdot C_6H_3Cl \cdot SCl,$$
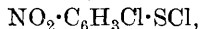
which forms golden-yellow needles, m. p. 98°. The latter is a highly reactive substance, and many of its derivatives are now described. The corresponding *bromothiol* forms brownish-yellow needles, m p. 111°.

The chlorothiol reacts with methyl alcohol to give different products under different conditions; when boiled with 75% alcohol, it yields the above disulphide, which is insoluble in the hot liquid, the sulphinic acid (below), which is soluble even in the cold, and 4-*chloro-2-aminobenzenesulphonic acid*, decomp. above 250°, which crystallises on cooling the filtrate. Potassium cyanide reacts with a hot acetic acid solution of the chlorothiol to give 4-*chloro-2-nitrophenyl thiocyanate*, pale yellow needles, m. p. 116—117°. On shaking with water and glass beads for several hours, the product is 4-*chloro-2-nitrothiophenyl oxide*, $O(S \cdot C_6H_3Cl \cdot NO_2)_2$, which crystallises in yellow tablets, blackens at 115—116°, explodes if heated rapidly, and closely resembles *o*-nitrothiophenyl oxide in its reactions (A., 1912, i, 763). Esters of the sulphinous acid, $NO_2 \cdot C_6H_3Cl \cdot S \cdot OR$, are obtained by the action of alcoholic or ethereal solutions of the sodium alkyl (or aryl) oxides; the *methyl* ester forms golden leaflets, m. p. 111—112°: the *ethyl* ester crystal-

lises in yellow needles, m. p. 73—74°; the *phenyl* ester forms nodules of stout, yellow needles, m. p. 75°.

4-*Chloro-2-nitrobenzenesulphinic acid*, $NO_2 \cdot C_6H_3Cl \cdot SO_2H$, slender, glistening leaflets, m. p. 127° (decomp.), is prepared by shaking the chlorothiol with $2N$-sodium hydroxide and acidifying the filtrate. Its silver salt reacts with methyl iodide to form the *methyl* ester, m. p. 143°, and with the chlorothiol to give 4:4′-*dichloro*-2 : 2′-*dinitrodiphenyl disulphoxide*, $S_2O_2(C_6H_3Cl \cdot NO_2)_2$, needles, m. p. 145°.

The chlorothiol reacts with ammonia in chloroform solution to give 4-*chloro-2-nitrophenylthiolamine*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot NH_2$, which crystallises in glistening, yellow leaflets, m. p. 126—127°, and resembles *o*-nitrophenylthiolamine in its reactions (*ibid.*). It forms a *benzylidene* compound, long, yellow needles. m. p. 161°, and when boiled with 50% acetic acid, changes into 4:4′-*dichloro*-2:2′-*dinitrodiphenyldithiolamine*, $NH(S \cdot C_6H_3Cl \cdot NO_2)_2$, slender, pale yellow needles, m. p. 210° (decomp.).

Towards phenols, the chlorothiol behaves like a diazonium chloride; phenol gives 4-*chloro-2-nitro-4′-hydroxydiphenyl sulphide*, yellow needles, m. p. 130°; α-naphthol forms 4-*chloro-2-nitrophenyl-2′-α-hydroxynaphthyl sulphide*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot C_{10}H_6 \cdot OH$, small, yellow tablets, m. p. 154—155°; β-naphthol yields a *sulphide* which crystallises in orange-yellow needles, m. p. 185°.

The chlorothiol also condenses with ketones. Acetone yields 4-*chloro-2-nitrophenylthiolacetone*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot CH_2 \cdot COMe$, yellow leaflets or broad needles, m. p. 114—115°; acetophenone gives *phenyl 4-chloro-2-nitrophenylthiolmethyl ketone*, pale yellow needles, m. p. 155°, which is oxidised by nitric acid to benzaldehyde and 4:4′-dichloro-2:2′-dinitrodiphenyl disulphide (above); ethyl acetoacetate or its copper compound forms *ethyl 4-chloro-2-nitrophenylthiolacetoacetate*, $NO_2 \cdot C_6H_3Cl \cdot S \cdot CHAc \cdot CO_2Et$, pale yellow tablets, m. p. 129—130°, decomp. 170°; acetylacetone yields *diacetyl-4-chloro-2-nitrophenylthiolmethane*,

$$NO_2 \cdot C_6H_3Cl \cdot S \cdot CH(COMe)_2,$$
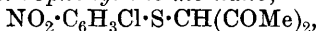
brilliant yellow, large needles, m. p. 116—117°. The acetophenone and acetoacetic ester compounds may be oxidised by perhydrol or chromic acid to *sulphoxides*; the *compound*,
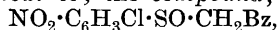
$$NO_2 \cdot C_6H_3Cl \cdot SO \cdot CH_2Bz,$$

forms pale yellow needles, m. p. 144°, and the *compound*, $NO_2 \cdot C_6H_3Cl \cdot SO \cdot CHAc \cdot CO_2Et$, stout, yellow tablets, m. p. 111°. They may also be reduced by means of stannous chloride, but the products are thiazine derivatives, and not amines. They separate as stannichlorides. 6-*Chloro-3-phenyl*-1 : 4-*benzothiazine* (annexed
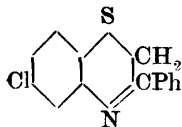
formula) crystallises in pale yellow, glistening tablets, m. p. 64°, and forms orange or red salts with the mineral acids, these being decomposed by water. The thiazine changes in a few days into a mixture of two compounds with the m. p.'s 178° and 241°; the change also proceeds in solution, acetic acid favouring the compound with

the higher m. p. and chloroform the other. The constitution is elucidated by the fact that the thiazine may be synthesised by the action of ω-bromoacetophenone on 4-chloro-2-aminothiophenol. *Ethyl 6-chloro-3-methyl*-1 : 4-*benzothiazine*-2-*carboxylate* crystallises in glistening, orange-red tablets or stout needles, m. p. 177—178°.

J. C. W.

Action of Formic Acid on the Triarylcarbinols. ADOLPHE KOVACHE (*Ann. Chim.*, 1918, [ix], **10**, 184—248).—A more detailed account of work already published (compare Guyot and Kovache, A., 1912, i, 186, 972; 1913, i, 647). W. G.

The Constitution of Dypnopinacone and its Derivatives. MAURICE DELACRE (*Ann. Chim.*, 1918, [ix], **10**, 101—137).—A theoretical discussion of work already published (compare A., 1914, i, 1068; 1916, i, 479). W. G.

The Hydrates and Alcoholates of Calcium Benzoate. FREDERICK STANBRIDGE (T., 1918, **113**, 808—816).—Anhydrous calcium benzoate combines with alcohol to form a *dialcoholate*, $(C_6H_5 \cdot CO_2)_2Ca,2C_2H_6O$, which crystallises in very small, transparent needles, and is very unstable.

When calcium benzoate trihydrate is treated with 95% (vol.) alcohol there is no action, but with 97% (vol.) alcohol the trihydrate is rapidly acted on. By the thermometric method, using 92·85% (weight) alcohol, it is found that the trihydrate rapidly changes at 35·5° into silky, oblong plates consisting of the monohydrate, $(C_6H_5 \cdot CO_2)_2Ca,H_2O$.

The solubility curve of calcium benzoate was determined, and it is shown that the trihydrate exists between $-0·37°$, the cryohydric point, and 84·7°. The latter temperature is a transition temperature, above which the monohydrate is probably the solid phase, although it could not be definitely isolated. The saturated solutions at the cryohydric and transition temperatures contain 2·22 and 7·62 grams of calcium benzoate, respectively, per 100 grams of water. Metastable portions of the solubility curves for both the trihydrate ·and monohydrate were obtained. The freezing-point curve of solutions of calcium benzoate of various strengths was also determined. T. S. P.

Preparation of Solutions of Mercuric Benzoate by means of Sodium Chloride. MARCEL DELÉPINE (*Bull. Sci. Pharmacol.*, 1917, **24**, 329—335; from *Chem. Zentr.*, 1918, i, 853).—Solutions of mercuric benzoate for subcutaneous injection, prepared by means of sodium chloride, contain a chlorine compound of mercury as the active constituent, and are therefore more simply obtained from the corresponding quantities of mercuric chloride, sodium benzoate, and sodium chloride, since in both cases the same equilibrium is reached in the solutions in consequence of the action of the sodium chloride on the mercuric benzoate. This view, first put forward by Varet on thermochemical grounds, is upheld by the fact that the two solutions contain the same quantity of mercury after being

shaken with ether. Solutions containing unchanged mercuric benzoate can be prepared by means of ammonium benzoate and ammonia; acetates and nitrates also have no action on the benzoate.

Mercuric benzoate, $(PhCO_2)_2Hg,H_2O$, is obtained by treating mercuric nitrate (225 grams in 1 litre of water) with sodium acetate (100 grams in 1 litre of water) and sodium benzoate (144 grams in 2 litres of water).   C. S.

Phthalic Acid Derivatives: Constitution and Colour. XIV. Some Derivatives of Tetrabromophthalimide. DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1415—1425).—In continuation of previous work, a series of derivatives of tetrabromophthalimide has been prepared (compare this vol., i, 167). In general, their properties closely resemble those of the tetrachloro- and tetraiodo-analogues, with the differences that might be expected from the substitution of bromine for chlorine or iodine.

Tetrabromophthalic anhydride, m. p. 279·5—280·5° (corr.), is prepared by the action of bromine on a hot solution of phthalic anhydride in fuming sulphuric acid in the presence of iodine; with dimethylaniline, it forms an additive *product*, $C_8O_3Br_4\cdot NMe_2Ph$, dark red crystals. *Tetrabromophthalimide*, small, yellow blades which decompose at about 300° and do not melt at 380°, is obtained by boiling a solution of the anhydride in nitrobenzene with formamide; it gives no colour when moistened with dimethylaniline.

The following series of derivatives was prepared by boiling a solution of the anhydride in glacial acetic acid with the requisite amine: *tetrabromophthalanil*, colourless plates with faint green cast, m. p. 279—280° (corr.): it gives a slight orange colour with dimethylaniline; *tetrabromophthal-o-tolil*, small, colourless plates, m. p. 291—293° (corr.); *tetrabromophthal-m-tolil*, almost colourless, glistening plates, m. p. 273·5—274·5° (corr.); *tetrabromophthal-p-tolil*, pale yellow needles, m. p. 280—280·5° (corr.), which crystallises from xylene with $\frac{1}{4}$ molecule of solvent of crystallisation; *tetrabromophthal-o-nitroanil*, fine, hair-like crystals, m. p. 289—298·5° (corr.; decomp.): it gives an additive *product* with dimethylaniline, crystallising in red, quadrilateral plates; *tetrabromophthal-m-nitroanil*, slender plates, m. p. 301·5—303° (corr.); *tetrabromophthal-p-nitroanil*, colourless needles, m. p. 331—331·5° (corr.); *tetrabromophthal-p-hydroxyanil*, short, yellow needles, m. p. 296—308° (corr.; decomp.): it separates from xylene with $\frac{1}{3}C_6H_4Me_2$; it gives an additive *compound* with dimethylaniline; *tetrabromophthal-p-acetylaminoanil*, minute, colourless needles, decomposing without melting at 381° (corr.); *tetrabromophthal-p-bromoanil*, minute blades with faint green colour, which do not melt at 380° (corr.); *tetrabromophthal-2:4-dibromoanil*, colourless prisms, m. p. 296—298·5° (corr.); *tetrabromophthal-2:6-dibromoanil*, nearly colourless, hexagonal crystals, m. p. 323·5—327° (corr.); *tetrabromophthal-2:4:6-tribromoanil*, colourless, diamond-shaped plates, m. p. 297—298° (corr.) (in these two cases, zinc

chloride is used as condensing agent); *tetrabromophthal*-p-*iodoanil*, bright yellow blades, decomposing without melting at about 381° (corr.); *tetrabromophthal*-3:4-*dimethylanil*, colourless plates, m. p. 264·5—271° (corr.); *tetrabromophthal*-2:4:5-*trimethylanil*, flat, colourless crystals, m. p. 307—308° (corr.); *tetrabromophthal*-o-*carboxyanil*, colourless prisms, m. p. 315·5—316·5° (corr.); *tetrabromophthal*-o-*ethoxyanil*, small, iridescent, light yellow plates, m. p. 247—248° (corr.); *tetrabromophthal*-p-*ethoxyanil*, light yellow crystals, m. p. 272·5—273° (corr.); *tetrabromophthal*-α-*naphthylimide*, light yellow needles, m. p. 309—309·5° (corr.); *tetrabromophthal*-β-*naphthylimide*, greenish-yellow plates, m. p. 305·5—308° (corr.); *tetrabromophthal*-p-*aminoazobenzene*, orange plates, m. p. 328·5—330° (corr.); *tetrabromophthalsemicarbazone*, short prisms with faint green tinge, which become red at 100°; *tetrabromophthalphenylhydrazone*, pale orange blades, m. p. 314—317·5° (corr.); *tetrabromophthalphenylethylhydrazone* separates from acetic acid in bright red needles, m. p. 211·0—211·5° (corr.), from benzene, ethyl acetate, or xylene in yellow needles, which become red at 95—96° and melt at the same temperature as the red variety. The crystals from benzene contain 1 mol. C_6H_6. The red variety becomes yellow when kept in a desiccator over benzene, and absorbs $\frac{2}{3}$ mol. C_6H_6; *tetrabromophthal*-2:4:6-*tribromophenylhydrazone* forms fine, hair-like needles, m. p. 290—291° (corr.); it appears to be unstable.   H. W.

Phthalic Acid Derivatives: Constitution and Colour. 3:4:6-Tri-iodophthaloxime and its Derivatives. DAVID S PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1425—1428).—The compounds were prepared with the object of investigating possible cases of dimorphism, such as had been observed with tetrachlorophthaloxime (this vol., i, 171), but not with phthaloxime or tetraiodophthaloxime (*loc. cit.*, i, 172).

3:4:6-*Tri-iodophthaloxime* has been prepared from tri-iodophthalic anhydride; it exists in only one form, long, lemon-yellow needles, m. p. 224—226° (decomp.). The *ammonium*, *sodium*, *potassium*, and *silver* salts are described. The following ethers are conveniently prepared by treating an alcoholic suspension of the silver salt with the requisite alkyl haloid: *methyl ether*, canary-yellow blades and needles, decomposing without melting at 245—253°; *ethyl ether*, pale yellow masses of confused, curved needles, m. p. 241·5—242·5°; iso*propyl ether*, yellow needles, m. p. 182—186°; *allyl ether*, coarse, deep yellow prisms, m. p. 192—192·5°; *benzyl ether*, glistening, yellow plates, m. p. 217—217·5°. The *acetate* forms pale yellow, lenticular blades, m. p. 223—224°; the *benzoate*, deep yellow, lenticular blades, m. p. 224—225°. All the temperatures recorded are corrected.   H. W.

The Nitration of 2- and 6-Methoxy-*m*-tolualdehydes and *m*-Toluic Acids. JOHN LIONEL SIMONSEN (T., 1918, **113**, 775—782).—In the hope of preparing 3-methoxy-4-methylphthalic

acid, the author has studied the nitration of 2-methoxy-*m*-tolualdehyde; the action, however, follows an unexpected course, and yields *5-nitro-2-methoxy-*m-*tolualdehyde*, needles, m. p. 61—62° (*semicarbazone*, fine, woolly needles, decomposing at 233°); the constitution of the aldehyde follows from its oxidation to *5-nitro-2-methoxy-*m-*toluic acid*, silky needles, m. p. 154°, which is also obtained by methylation of the corresponding hydroxy-acid (Einhorn and Pfyl, A., 1900, i, 439) and by nitration of 2-*methoxy-*m-*toluic acid*, hair-like needles, m. p. 83° (the *silver* salt forms a caseous, white precipitate).

6-Methoxy-*m*-tolualdehyde is converted by nitric acid into *5-nitro-6-methoxy-*m-*tolualdehyde*, needles, m. p. 77° (*semicarbazone*, needles, decomposing at 235°), which is readily oxidised to *5-nitro-6-methoxy-*m-*toluic acid*, felted needles, m. p. 180—181° (the *barium*, *calcium*, and *silver* salts, and the *methyl* ester, needles, m. p. 47°, are described). The same acid, together with a *substance*, probably 6-*nitro-o-tolyl methyl ether*, m. p. 69°, is obtained by nitration of 6-methoxy-*m*-toluic acid. The constitution of the ether is deduced from its oxidation to 6-*nitro-2-methoxybenzoic acid*, m. p. 161°, but the quantity of the latter which was available did not permit an extended investigation.

5 : 5′-*Dinitro*-2 : 2′-*dimethoxydi-3-methylstyryl ketone*, fine, yellow needles, decomposing at 252°, and 5 : 5′-*dinitro*-4 : 4′-*dimethoxydi-3-methylstyryl ketone*, yellow needles, m. p. 214°, are prepared from the corresponding aldehydes.   H. W.

Preparation of 1-Monohydroxy- and 1 : 8-Dihydroxy-anthranol. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 305886; additional to D.R.-P. 296091; from *Chem. Zentr.*, 1918, ii, 238).—The alkyl ethers of 1-hydroxy- and 1 : 8-dihydroxy-anthraquinones are reduced by zinc in acid solution in the place of the parent substances (compare this vol., i, 111). The methyl ethers are cited as examples.   H. W.

Morindone. JOHN LIONEL SIMONSEN (T., 1918, **113**, 766—774). —Although certain unexplained discrepancies exist between the results of Oesterle and Tisza (A., 1908, ii, 527) and Perkin and Hummel (T., 1894, **65**, 851), the author considers morindone obtained from *Morinda citrafolia* to be identical with that derived from *M. umbellata*.

Morindone is probably a hydroxymethylanthrarufin (I) or a hydroxymethylchrysazin (II) (annexed formulæ), for the following reasons. The methyl group is in position 2, since morindone can be converted into 2 - methylanthracene (Perkin and Hummel, *loc. cit.*). Morindone contains three hydroxy-groups, since it yields triacetyl, tribenzoyl   (yellow
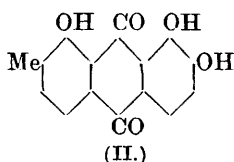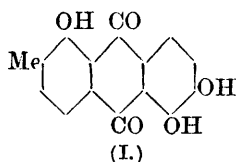
(I.)

(II.)

needles, m. p. 218—219°), and trimethyl derivatives.   Two of the hydroxy-groups must be in the ortho-position with respect to the carbonyl groups of the anthraquinone nucleus, since treatment with methyl iodide and alkali only yields a monomethyl *ether*, brown needles, m. p. 248°.   Further, morindone is a mordant dye resembling alizarin, and hence probably has two of the hydroxy-groups in the 1 : 2-position.   The hydroxy-group, which undergoes methylation with methyl iodide, must be present in the same ring as another hydroxy-group, since morindone monomethyl ether is completely destroyed on oxidation.   Morindone cannot be a derivative of anthragallol or purpurin, since it is perfectly stable in alkaline solution.   Hence it follows that the only positions for the hydroxyl groups are as in 1 : 5 : 6- or 1 : 7 : 8-trihydroxyanthraquinone.

Further, it is highly probable that the methyl group is in the ortho-position with respect to one of the hydroxyl groups, since all attempts to oxidise it to a carboxyl group failed.   Four formulæ are thus possible, of which the two quoted above are most probable, preference being given to (I), since morindone resembles more closely hydroxyanthrarufin than hydroxychrysazin in its colour reactions.

The presence of a –$CH_2 \cdot OH$ group in morindone, as suggested by Perkin (Thorpe's Dictionary, III, 547), is unlikely.

Attempts to isolate in a pure state the sugar obtained by the hydrolysis of morindin were unsuccessful.   H. W.

Complete Synthesis of Norcamphor.   S. V. HINTIKKA and GUST. KOMPPA (*Ann. Acad. Sci. Fennicae*, 1918, [*A*], **10**, No. 22, 1—12; from *Chem. Zentr.*, 1918, ii, 369—370).—Ethyl*cyclo*pentane-1-one-2-carboxylate is condensed by heating with zinc in benzene solution with methyl bromoacetate to *ethyl methyl hydroxyhomonorcamphorate* (annexed formula), a viscous, colourless oil, b. p. 140—172°/14 mm., which is converted by heating with sodium hydrogen sulphate at 120—140° into *methyl ethyl dehydrohomonorcamphorate*, $C_{11}H_{16}O_4$, a colourless oil, b. p. 143—145°/12 mm., D_4^{17} 1·09078, n_D 1·46956.   On reduction

$$CH_2 \cdot CH \cdot CO_2Et$$
$$| \quad CH_2$$
$$|$$
$$CH_2 \cdot C(OH) \cdot CH_2 \cdot CO_2Me$$

with hydrogen and colloidal platinum, the latter yields *methyl ethyl homonorcamphorate*, b. p. 135—141°/13 mm., D_4^{17} 1·06829, n_D 1·45054.   The corresponding *acid* separates from water in monoclinic prisms, from ether in radiating needles, and has m. p. 137—137·5° (corr.).   The *lead* salt is crystalline; the *anilide* forms needles, m. p. 195—198·5°.   *Norcamphor* is obtained in the form of readily volatile crystals, m. p. 93—94°, by dry distillation of the above-mentioned lead salt in an atmosphere of carbon dioxide; the *semicarbazone* has m. p. 196·5—197·5°.

Attempts to prepare norcamphor from *cyclo*pentanedicarboxylic anhydride failed, on account of the difficulty of obtaining the latter in requisite quantity.   In another series of experiments, lack

of success was due to inability to effect a normal hydrolysis or reduction of *ethyl cyanodehydrohomonorcamphorate*, $C_{13}H_{27}O_4N$, colourless oil, b. p. 189°/10 mm. (obtained by condensation of ethyl *cyclo*pentan-1-one-3-carboxylate with ethyl cyanoacetate in the presence of diethylamine), to homonorcamphoric acid.

<div align="right">H. W.</div>

Conversion of Menthone into Pulegenone. O. WALLACH

and E. GROTE (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 319—333; from *Chem. Zentr.*, 1918, ii, 120—121).—It has been shown previously (A., 1916, i, 487) that in the transformation of the dibromides of *cyclo*hexanones into *cyclo*pentanones, intermediate compounds of the general formula $C_nH_{2n-4}O_2$ are obtained which are regarded as hydroxy-ketones, and can be further converted into *cyclo*pentanehydroxycarboxylic acids and *cyclo*pentanones. In this manner, menthone yields two isomeric compounds, $C_{10}H_{16}O_2$ (α-compound, m. p. 82—83°, β-compound, m. p. 36—38°), of which the α-isomeride proves to be identical with buchu-camphor. These compounds have now been further investigated.

The two substances, $C_{10}H_{16}O_2$, appear to behave similarly towards bromine; a mixture of them is converted by this reagent in acetic acid solution into a monobromide, $C_{10}H_{15}O_2Br$, m. p. 77—78°, identical with the monobromobuchu-camphor described by Cusmano (A., 1914, i, 303). When warmed with anhydrous pyridine or sodium hydroxide solution, the monobromide yields hydroxythymoquinone. A second *monobromide*, $C_{10}H_{15}O_2Br$ (?), yellow crystals, m. p. 100—101°, or possibly somewhat higher (decomp.), is prepared by brominating in acetic acid solution at 60°. The *dibromide*, $C_{10}H_{14}O_2Br_2$, yellow crystals with green glance, m. p. 44—45°, is obtained by the action of an excess of bromine on an ethereal solution of the monobromide, m. p. 77°, or of buchu-camphor; it is not decomposed by boiling acetic acid, and is reduced by acetic acid and zinc dust to buchu-camphor; when warmed with pyridine, it yields a colourless oil, the alkaline solution of which is oxidised by air to hydroxythymoquinone. Aqueous potassium hydroxide transforms the dibromide into an *acid*, $C_{10}H_{18}O_5,H_2O$, transparent prisms, m. p. 88—89°, the *silver* salt of which is described. This acid, on dry distillation, yields pulegenone (methyl*iso*propyl-Δ³-*cyclo*penten-2-one), b. p. 188·5—189°, n_D^{20} 1·4660 (semicarbazone, m. p. 183—184°). The ketone is reduced by hydrogen in the presence of palladium to dihydrocamphorphorone.

The previously described compound, $C_7H_{10}O_2$ (from the dibromide of methyl*cyclo*hexan-2-one, *loc. cit.*), is converted by excess of bromine in ethereal solution into a *tribromide*, $C_7H_7O_2Br_3$, yellow, hexagonal plates, m. p. 115—116°, which dissolves in alkali, yielding an acid containing bromine.

<div align="right">H. W.</div>

New Synthetic Glucosides. FERDINAND MAUTHNER (*J. pr.

Chem.*, 1918, [ii], **97**, 217—224. Compare A., 1912, i, 574; 1914, i, 195).—A solution of acetovanillone in aqueous sodium hydroxide

and acetone is treated below 18° with an acetone solution of aceto-bromoglucose, whereby *tetra-acetylglucoacetovanillone*, $C_{23}H_{28}O_{12}$, colourless crystals, m. p. 156—157°, is obtained, which yields by hydrolysis with 6% barium hydroxide solution *glucoacetovanillone*, $C_{15}H_{20}O_8$, colourless needles, m. p. 223—224°.

In a similar manner, the following glucosides have been prepared: *methyl tetra-acetylglucosalicylate (tetra-acetylgaultherin)*, $C_{22}H_{26}O_{12}$, colourless leaflets, m. p. 154—155°, from methyl salicylate; *methyl tetra-acetylgluco-p-coumarate*, $C_{24}H_{28}O_{12}$, colourless crystals, m. p. 160—161°, from methyl *p*-coumarate (*gluco-p-coumaric acid*, $C_{15}H_{18}O_8$, forms colourless needles, m. p. 194—195°); *methyl tetra-acetylglucoferulate*, $C_{25}H_{30}O_{13}$, colourless needles, m. p. 125—126°, from methyl ferulate (*glucoferulic acid*, $C_{16}H_{20}O_9$, forms colourless needles, m. p. 186—187°). C. S.

Conversion of Mannitol into Methyl-α-pyran. A. WINDAUS and A. TOMICH (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 462—468; from *Chem. Zentr.*, 1918, ii, 109).—It has been shown by Fauconnier (A., 1885, 743) that mannitol is converted by formic acid into mannitan, $C_6H_{12}O_5$, and *iso*mannide, $C_6H_{10}O_4$; the former is esterified by formic acid, yielding a diformate which, at 210°, undergoes decomposition according to the schemes:

$$C_6H_{10}O_3(O \cdot COH)_2 = CO + CO_2 + C_6H_{12}O_4$$

and $C_6H_{10}O_3(O \cdot COH)_2 = 2H_2O + 2CO_2 + C_6H_8O$. The latter substance, C_6H_8O, has been obtained in a different manner by the authors. Closer investigation shows it to be methyl-α-pyran (annexed formula), since it passes into δ-hexylene oxide (compare Lipp, A., 1886, 219) when reduced by hydrogen in the presence of spongy palladium. The identity of products is further proved by converting each into the same dibromide, $C_6H_{12}Br_2$. H. W.

Derivatives of Berberine Closely Allied to Derivatives of Cryptopine. WILLIAM HENRY PERKIN, jun. (T., 1918, **113**, 722—765).—The close relationship which exists between cryptopine and berberine has been previously discussed (T., 1916, **109**, 833, 841; 1918, **113**, 493); the object of the present investigation was to introduce an *N*-methyl group into the berberine molecule in order to study derivatives of berberine which are similarly constituted to the corresponding derivatives of cryptopine, and only differ from these in containing the two methoxy-groups and the methylenedioxy-group in the reversed positions.

The views of Gadamer (A., 1911, i, 152) with regard to the identity of dihydroanhydroberberine are substantially confirmed (compare Faltis, A., 1910, i, 698).

Dihydroanhydroberberine methosulphate, brilliant yellow, ortho-rhombic prisms, m. p. 205°, is converted into the *methochloride*, m. p. 223°, which, similarly to *iso*cryptopine chloride, is transformed into *anhydromethylberberine*, pale yellow prisms, m. p.

94—95°; the latter, on reduction, yields *N*-methyl*iso*tetrahydro-anhydroberberine (Pyman, T., 1913, **103**, 827).

The behaviour of anhydromethylberberine and anhydrocrypto-pine with concentrated hydrochloric acid shows points of difference, but with the dilute acid the actions are very similar; thus, anhydro-methylberberine gives two, probably stereoisomeric, *hydroxyiso-anhydrodihydromethylberberines*, m. p.'s 210—212° and 168—170°, respectively. These are converted by acetyl chloride into mixtures of the *hydrochlorides* of two acetoxy*iso*anhydrodihydromethyl-berberines, from which the *acetyl* bases, m. p.'s 165—167° and 213—215°, respectively, are obtained.

iso*Anhydromethylberberine*, m. p. 123—124°, is prepared from either modification of hydroxy*iso*anhydrodihydromethylberberine; it yields a *hydrochloride*, m. p. 205—210°, and a *hydriodide*, m. p. 247°.

The reduction of dihydroanhydroberberine methochloride leads to the formation of the two modifications of the methochloride of tetrahydroanhydroberberine on the one hand, and of *dihydro-methyliso*tetrahydroanhydroberberine on the other (compare Pyman, T., 1913, **103**, 823); the methosulphate of the latter can be converted into *dihydrodimethyliso*tetrahydroanhydroberberine. This substance similarly yields a methosulphate, from which *berberidene* (annexed formula), m. p. 113—114°, is derived. The main evidence in support of the formula is obtained by a study of the oxidation of the substance; it yields 5:6-dimeth-oxy-*o*-tolualdehyde, 5:6-dimeth-oxy-*o*-toluic acid, and an acid, m. p. 174—176°, which is doubtless hydrastic acid.
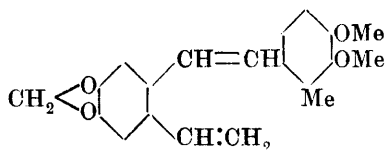
Anhydromethylberberine methosulphate, colourless needles, m. p. 150—152° (*methiodide*, m. p. 188—190°), resembles anhydro-cryptopine methosulphate, in that it is converted by methyl-alcoholic potassium hydroxide into anhydromethylberberine; it is transformed by hydrochloric acid into ψ-*methylberberinium chloride*, m. p. 95—100° (*iodide*, m. p. 175—180°), which closely resembles ψ-cryptopine chloride.

Oxyberberine is readily reduced electrolytically to tetrahydro-anhydroberberine, thus completing the synthesis of berberine devised by Pictet and Gams (A., 1911, i, 807).

For experimental details, the original must be consulted.

H. W.

Preparation of Hydrogenated Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 306939; from *Chem. Zentr.*, 1918, ii, 421).— Alkaloids or their salts can be smoothly hydrogenated in aqueous solution or suspension by means of molecular hydrogen in the presence of nickel suboxide; the temperature may be normal or somewhat above (up to 60°), and the pressure normal or slightly

raised. Thus, hydroquinine and dihydromorphine are prepared from quinine hydrochloride and morphine, respectively, whilst cinnamylcocaine gives *hydrocinnamylcocaine*, an oily liquid which is decomposed by heat. H. W.

Pyrrole Blacks. A. ANGELI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 209—212; *Gazzetta*, 1918, **48**, ii, 21—25. Compare A., 1915, i, 9913.—As well as by the action of hydrogen peroxide in acetic acid solution, pyrrole is converted by most oxidising agents into highly coloured products, mostly black or brown, some being readily soluble and others insoluble in alkalis. Thus, addition of potassium dichromate to an acetic acid solution of pyrrole immediately precipitates an intensely black powder, and if a cotton fabric is soaked in the acid pyrrole solution and then transferred to the dichromate bath, it is dyed black, the colour being very fast against soap and light. This colouring matter contains chromium, probably combined, at least partly, with the colouring matter in the form of a lake. When treated with dilute sulphuric acid and dichromate, the black material passes into solution, and from the solution ether extracts maleimide, so that its molecule still contains pyrrole residues. It is probable that the series of changes: pyrrole $\longrightarrow$ pyrrole black $\longrightarrow$ maleimide is analogous to: aniline $\longrightarrow$ aniline black $\longrightarrow$ quinone.

The formation of pyrrole black seems to be preceded by polymerisation of the pyrrole molecule, this taking place with greater or less rapidity according to the reagents employed. The possible structures of these polymerides, their relation to the colouring matters, and the connexion of the latter with the black compounds formed as a result of the action of tyrosinase, are discussed.

T. H. P.

Pyrrole Blacks and Melanins. A. ANGELI (*Atti R. Accad. Lincei*, 1908, [v], **27**, i, 417—421).—In connexion with the close analogy between pyrrole blacks and natural melanins, as regards method of formation and also characters and behaviour (preceding abstract), the author directs attention to a number of cases of formation, either in the animal organism or through the agency of animal products, of dark pigments from pyrrole derivatives, and also from adrenaline, tyrosine, and hydroxyphenylethylamine, these compounds having skeletons similar to that of pyrrole.

T. H. P.

The Compounds of Phenol and the Cresols with Pyridine. II. F. W. SKIRROW and T. V. BINMORE (*J. Amer. Chem. Soc.*, 1918, **40**, 1431—1442. Compare Hatcher and Skirrow, A., 1917, i, 665) —The effect of excess of phenol and excess of pyridine on the dissociation of pyridine-phenol, postulated as $C_6H_5 \cdot OH, C_5H_5N \rightleftharpoons C_6H_5 \cdot OH + C_5H_5N$, has been studied by the cryoscopic method, and it has been found that phenol depresses the dissociation much more strongly than does pyridine. The dominant equilibrium might

therefore be $(C_6H_5\cdot OH)_2,C_5H_5N \rightleftharpoons 2C_6H_5\cdot OH + C_5H_5N$, but a study of this dissociation on similar lines showed that the effect of excess of phenol on the apparent dissociation was only greater than the effect of excess of pyridine with comparatively high additions of these. An explanation of these results and of the extraction results of the earlier paper is based on the following equilibria: $C_6H_5\cdot OH,C_5H_5N \rightleftharpoons C_6H_5\cdot OH + C_5H_5N$ and $C_6H_5\cdot OH,C_5H_5N + C_6H_5\cdot OH \rightleftharpoons (C_6H_5\cdot OH)_2,C_5H_5N$.

It is shown that the difference between the effect of addition of excess of phenol and of excess of pyridine in the extraction experiments tends to disappear as the dilution of the benzene solution is increased.   H. W.

Preparation of Derivatives of Hydroxyarylquinolinedicarboxylic Acids. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 305885; additional to D.R.-P. 293467; from *Chem. Zentr.*, 1918, ii, 237).—Derivatives of isatic acid, substituted in the nucleus, are condensed with acetylsalicylic or acetylcresotic acids. Thus, *hydroxytolylquinolinedicarboxylic acid*, orange powder, decomposing above 280°, is prepared by warming 5-methylisatin with *p*-acetylsalicylic acid in the presence of potassium hydroxide and water. Similarly, 5:6-methylenedioxyisatin and *p*-acetylsalicylic acid yields a *quinolinedicarboxylic acid*, yellow powder. The product obtained from 5-methylisatin and acetyl-*p*-cresotic acid is a yellowish-red *powder* which decomposes at 290°. 6-*Bromo*-4′-*hydroxyphenylquinoline*-4:3′-*dicarboxylic acid*, yellow powder, decomposing at about 273°, results from 5-bromoisatin and *p*-acetylsalicylic acid.   H. W.

N-**Acyl Derivatives of Carbazole.** MAURICE COPISAROW (T., 1918, **113**, 816—820).—Good yields of *N*-acylcarbazoles are obtained by triturating potassium carbazole with a slight excess of the requisite acid chloride; the energy of reaction and the stability of the products decrease with the complexity of the acyl group in the case of monobasic acids.

The action has been studied in the cases of acetyl, benzoyl, phenoxyacetyl, *n*-nonoyl, palmityl, carbonyl, and oxalyl chlorides.

It is improbable that *N*-oxalylcarbazole is an intermediate product in the formation of "carbazole-blue."

For experimental details, the original paper must be consulted.   H. W.

Preparation of Piperazine. DAVID S. PRATT and CHARLES O. YOUNG (*J. Amer. Chem. Soc.*, 1918, **40**, 1428—1431. Compare D.R.-P. 60547).—The following process has proved satisfactory, but may be capable of improvement on a manufacturing scale. A mixture of ethylene bromide, aniline, and anhydrous sodium carbonate is heated to gentle boiling for five to six hours, the warm fused mass is extracted with hot water, and the crude diphenylpiperazine transformed into its nitroso-derivative by suspending it in cold concentrated hydrochloric acid and gradually adding a satu-

rated solution of sodium nitrite through a tube reaching to the bottom of the acid. The precipitate, probably the hydrochloride of dinitrosodiphenylpiperazine, is added to a 40% solution of sodium hydrogen sulphite and the suspension warmed to about 80°; the solution is made strongly alkaline with sodium hydroxide and concentrated by distillation. The piperazine is finally isolated by distillation of the residue with superheated steam and is absorbed by hydrochloric acid.

Traces of piperazine are conveniently detected by means of platinic chloride, picric acid, or bismuth potassium iodide (brilliant garnet crystals), or by the formation of dinitrosopiperazine.

H. W.

Formulation of so-called Quinonoid Dyes. HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, 1, 210—218).—The authors propose to apply, with certain modifications, Werner's views of the structure of inorganic compounds to quinonoid dyes, and to formulate these as complex compounds. Thus, rosaniline chloride is represented by the formula
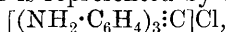
$$[(NH_2 \cdot C_6H_4)_3 : C]Cl,$$

and similar formulæ are given for dyes of the diphenylmethane, azine, thiazine, oxazine, and xanthene classes. The conversion of a coloured "ammonium" base into a colourless carbinol is represented by the formulæ $[(NH_2 \cdot C_6H_4)_3 : C]OH \longrightarrow$

$$(NH_2 \cdot C_6H_4)_3 : C \cdot OH,$$
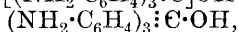
the hydroxyl group being attached definitely to the carbon atom instead of indefinitely to the whole complex. The colour changes produced by mineral acids in aqueous solutions of triphenylmethane dyes find a simple explanation if the assumption is made that with increasing concentration of the acid molecules of the acid enter the complex and modify the auxochromic influence of the amino- or substituted amino-groups. C. S.

Explanation of Heumann's Rosaniline Synthesis. HANS EDUARD FIERZ and HARTMANN KOECHLIN (*Helv. Chim. Acta*, 1918, 1, 218—226).—In the original Heumann reaction (D.R.-P. 66511 and 68976), carbon tetrachloride and a tertiary amine, for example, dimethylaniline, are made to react in the presence of aluminium chloride, whereby crystal-violet or an analogous product is at once obtained. The authors state that the primary product is the keto-chloride, $CCl_2(C_6H_4 \cdot NMe_2)_2$ (although they have not succeeded in isolating it), because the reaction product, after heating at 50° has been continued for ten minutes, yields a small quantity of Michler's ketone when added to ice-water. When acetanilide is used instead of dimethylaniline, and the temperature not allowed to exceed 30° during the reaction, a 60% yield of 4 : 4'-diaminobenzophenone is obtained on adding the reaction product to ice-water and hydrolysing the product with dilute sulphuric acid (1 : 1) at 110—115°.

4 : 4'-Diaminobenzophenone, which thus becomes an easily obtainable substance, forms a *diacetyl* derivative, colourless needles,

m. p. 237°, a *dibenzylidene* derivative, colourless needles, m. p. 194°, and a *phenylhydrazone*, faintly rose-coloured needles, m. p. 240°. 3 : 3′-*Dichloro*-4 : 4′-*diaminobenzophenone*, a yellow, crystalline powder, is obtained from *o*-chloroacetanilide, and 4 : 4′-tetramethyldiamino-2 : 2′-dimethylbenzophenone from dimethyl-*m*-toluidine in a similar manner.

Tetrazotised diaminobenzophenone couples with β-naphthol and with naphthol A.S. to produce bisazo-dyes of little interest.

The keto-chloride obtained from acetanilide reacts with dimethylaniline to produce 4-*dimethylamino*-4′ : 4″-*diacetylaminotriphenylmethyl chloride*, $NMe_2 \cdot C_6H_4 \cdot CCl(C_6H_4 \cdot NHAc)_2$, which dyes silk and wool grey; after hydrolysis of the acetyl groups, the resulting base dyes silk and wool violet.

The keto-chloride obtained from dimethyl-*m*-toluidine reacts with a further quantity of the same base to produce hexamethyltriaminotri-*m*-tolylmethyl chloride, which dyes silk and wool in pure blue tones.   C. S.

Naphthasultam. III. Nitro- and Amino-derivatives of Naphthasultam, and Hydrolytic Products of Tetrachloroketotetrahydronaphthasultam [2 : 2 : 3 : 3-Tetrachloro-1 : 8-naphthasultam-4-quinone]. Th. Zincke and Grete Schürmann (*Annalen*, 1918, **416**, 65—85. Compare A., 1916, i, 426; 1917, i, 38).—The analogy between 1 : 8-naphthasultam and α-naphthol is also exhibited by their nitro- and amino-derivatives.

When 1 : 8-naphthasultam is ground with nitric acid (D 1·2; 10 parts), it yields 2 : 4-*dinitro*-1 : 8-*naphthasultam*, $C_{10}H_5O_6N_3S$, in brownish-yellow tablets and prisms, m. p. 258° (decomp.), and forms deep yellow, crystalline ammonium, potassium, and sodium salts. Dannerth (A., 1907, i, 909) regarded the product as a mononitro-derivative. On reduction with tin and hydrochloric acid, the compound gives 2 : 4-*diamino*-1 : 8-*naphthasultam*; this crystallises in slender, yellow needles, which soon become dark on exposure to the air, and forms a *monohydrochloride*, yellow needles, a *dihydrochloride*, pale yellow needles, and a *triacetyl* derivative, white needles, m. p. above 270°, which changes into 2 : 4-*diacetylamino*-1 : 8-*naphthasultam*, $C_{14}H_{13}O_4N_3S$, when shaken with dilute alkali hydroxide (compare Dannerth, *ibid.*). The hydrochlorides are oxidised by ferric chloride to 2-*amino*-1 : 8-*naphthasultam*-4-quinoneimide (annexed formula), a reddishbrown powder, which blackens at 230—235°, and forms a *hydrochloride*, dark red needles. The imide reacts with aniline in hot alcoholic acetic acid to give 2-*anilino*-1 : 8-*naphthasultamquinoneanil*, $C_{22}H_{15}O_2N_3S$, which crystallises in bronzy-red needles, m. p. 235—236° and forms an almost black hydrochloride and nitrate.

N—SO₂ / NH₂ / NH
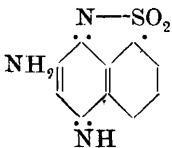
2 : 2 : 3 : 3-Tetrachloronaphthaquinone and 2 : 2 : 3 : 3-tetrachloro-1 : 8-naphthasultam-4-quinone resemble each other in their behaviour towards alkalis. If the latter is triturated for a few

minutes with aqueous-alcoholic sodium hydroxide, it is hydrolysed to *2-trichloroacrylyl-3-sulphamidobenzoic acid*,

$$CCl_2{:}CCl{\cdot}CO{\cdot}C_6H_3(CO_2H){\cdot}SO_2{\cdot}NH_2,$$
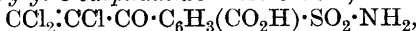
which crystallises in stout tablets from dilute alcohol or long needles from dilute hydrochloric acid, has m. p. 197—198° (decomp.), and forms a *methyl* ester, stout prisms and tablets, m. p. 115—116°. Both the acid and the ester deposit trichloro-ethylene on shaking with alkali hydroxide, the solution containing the salt of *phthalic-sulphinide* ("*saccharincarboxylic acid*") (annexed formula). This acid may be obtained directly from the quinone by prolonging the action of alkali to two hours, the hydrolysis and subsequent reactions being represented as follows :
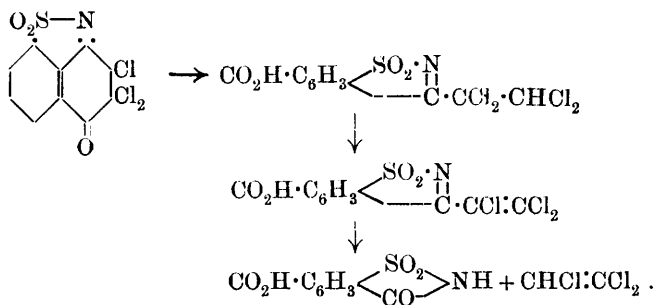
Phthalicsulphinide crystallises in stout, hard needles, m. p. 275—276°, and whilst it is stable towards dilute alkalis, it is readily hydrolysed by boiling with dilute hydrochloric acid to *3-sulphamidophthalic acid*, $NH_2{\cdot}SO_2{\cdot}C_6H_3(CO_2H)_2$, which crystallises with $1H_2O$ in glistening leaflets or broad needles, m. p. 165° (decomp.), the anhydrous acid having m. p. 194°, and changing at this temperature, or when warmed with concentrated sulphuric acid, into phthalicsulphinide. The acid is stable towards boiling N-alkali hydroxide, but its *methyl* ester, glistening leaflets, m. p. 139°, changes into phthalicsulphinide when shaken with alkali hydroxide in the cold. Conversely, phthalicsulphinide yields this methyl ester when warmed with methyl-alcoholic hydrogen chloride. These derivatives of phthalic acid were originally described by Comstock (1883), Stokes (1884), and Moulton (1891), working under Remsen's guidance, but they failed to differentiate clearly between phthalicsulphinide and sulphamidophthalic acid.

J. C. W.

Analogies in Behaviour between the Diazoimide and Diazomethane Rings. E. OLIVERI-MANDALÀ (*Gazzetta*, 1918, **48**, ii, 35—39).—A very brief summary of the principal results of a number of papers published in the years 1910—1915. T. H. P.

Electrolytic Reduction of Hydroxyazo-compounds. E. PUXEDDU (*Gazzetta*, 1918, **48**, ii, 25—30).—In alcoholic solution

and in presence of hydrochloric acid, *p*-hydroxyazobenzene undergoes electrolytic reduction to *p*-aminophenol, whereas in presence of sulphuric and acetic acids no definite result is obtained.

<div align="right">T. H. P.</div>

Aromatic Nitro-derivatives. VII. Formation of Nitrohydrazo compounds. MICHELE GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 247—252; *Gazzetta*, 1918, **48**, ii, 8—17).—By the action of phenylhydrazine on trinitrotolylmethylnitroamine and on trinitromethyl-*p*-toluidine, Sommer (A., 1903, i, 655) obtained derivatives of hydrazobenzene. With aromatic polynitro-compounds containing a labile nitro-group, phenylhydrazine in the cold exerts not a reducing, but rather a substituting action. The author finds that this behaviour of phenylhydrazine is general in character, and furnishes a good method for preparing nitrohydrazo-compounds.
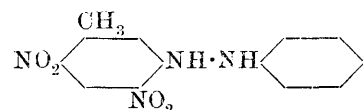
2 : 4-*Dinitro-5-methylhydrazobenzene* (annexed formula), obtained by the action of phenylhydrazine on 2:4:5-trinitrotoluene in methyl-alcoholic solution, forms reddish-yellow plates, m. p. 155° (decomp.). When treated in alcoholic solution with gaseous hydrogen chloride, it is converted into 4-*nitro*-2-*nitroso*-5-*methylazobenzene* (annexed formula), which crystallises in golden-yellow plates, m. p. 120—121°.

2 : 6-*Dinitro-5-methylhydrazobenzene*, $C_{13}H_{12}O_4N_4$, obtained from phenylhydrazine and 2:3:4-trinitrotoluene, forms large, red prisms, m. p. 137° (decomp.), and by gaseous hydrogen chloride in alcoholic solution is converted into 6-*nitro-2-nitroso-5-methylazobenzene* or 2-*nitro-6-nitroso-5-methylazobenzene*, $C_{13}H_{10}O_3N_4$, which crystallises in shining, yellow needles, m. p. 154°.

<div align="right">T. H. P.</div>

Aromatic Nitro-derivatives. Formation of Nitrohydrazo-compounds. MICHELE GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 379—382. Compare preceding abstract).—2′ : 4′-*Dinitrobenzeneazo*-m-*benzoic acid* (annexed formula), prepared, together with a brown compound, m. p. below 100°, by the action of phenylhydrazine on 2:4:5-trinitrobenzoic acid, forms yellow needles, m. p. 135° (decomp.); its *silver* salt was analysed. When dissolved in methyl alcohol and treated with gaseous hydrogen chloride, it yields 4′-*nitro-2′-nitrosobenzene*-m-*azobenzoic acid* (annexed formula), which crystallises in golden-yellow needles, m. p. 244° (decomp.).
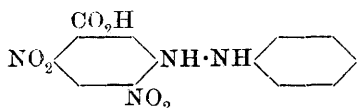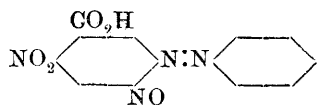
Methyl 2′ : 4′-*dinitrobenzenehydrazobenzoate*, $C_{14}H_{12}O_6N_4$, obtained from phenylhydrazine and methyl

2:4:5-trinitrobenzoate, forms shining, orange-red plates, m. p. 177—178° (decomp.); from methyl alcohol containing benzene, it crystallises along with an *isomeride*, which forms pale yellow, prismatic crystals, m. p. 147°; these begin to emit gas at 175—178°.

In the action of *as*-phenylmethylhydrazine on 2:4:5-trinitrotoluene, a similar substitution takes place, with elimination of nitrous acid and subsequent formation of nitrogen.   T. H. P.

Hydrazino-acids. II. AUGUST DARAPSKY (*J. pr. Chem.*, 1918, [ii], **97**, 182—217. Compare *ibid.*, 1917, [ii], **96**, 251).—In addition to the five methods of preparing hydrazino-acids already described (*loc. cit.*), the author has examined the behaviour of mandelonitrile with hydrazine hydrate, and found that the reaction does not follow the expected course. A violent reaction ensues when the mixture is warmed on the water-bath, ammonia and hydrogen cyanide are evolved, and the dark red liquid deposits a small quantity of a substance, pale yellow leaflets, m. p. about 175°, which is not individual and probably contains diphenyldihydrotetrazine, since it yields diphenyltetrazine by oxidation. When the reaction proceeds in cold alcoholic solution, dibenzenylhydrazidine (Pinner, A., 1898, i, 94) is obtained; no trace of Purgotti's α-toluonitrile (A., 1895, i, 602) could be detected.

The behaviour of benzaldehyde towards hydrazine monohydrochloride and potassium cyanide is exactly analogous to that of formaldehyde (Jay and Curtius, A., 1894, i, 162). When equal molecular quantities of the three substances react in cold aqueous methyl-alcoholic solution, *α-benzylidenehydrazinophenylacetonitrile*, CHPh:N·NH·CHPh·CN, yellow leaflets, m. p. 112°, is obtained. If two molecules of benzaldehyde are used, or if hydrazine dihydrochloride is employed instead of the monohydrochloride, the product is benzylideneazine, a small amount of a by-product, colourless needles, m. p. 215°, being obtained in both cases. The α-benzylidenehydrazinophenylacetonitrile is probably formed from benzylidenehydrazine and mandelonitrile, the initial products of the reaction, since it is shown that these two substances react to produce the first under the experimental conditions. α-Benzylidene-hydrazinophenylacetonitrile yields hydrogen cyanide, benzaldehyde, and hydrazine by hydrolysis with hot 20% hydrochloric acid, and *α-benzylidenehydrazinophenylacetamide*, colourless crystals, m. p. 165—167° (decomp.), by treatment with concentrated hydrochloric acid at the ordinary temperature. When the amide is treated with *N*-hydrochloric acid and an equal volume of water, and the mixture is distilled with steam, *α-hydrazinophenylacetamide hydrochloride*, $NH_2 \cdot CO \cdot CHPh \cdot NH \cdot NH_2, HCl$, colourless leaflets, m. p. 215° (decomp.), is obtained, which can be converted into *α-benzylidene-hydrazinophenylacetic acid*, $C_{15}H_{14}O_2N_2$, long needles, m. p. 150°, and into *α-hydrazinophenylacetic acid*, colourless leaflets, m. p. 188—189°.

The preceding reaction between benzaldehyde, hydrazine mono hydrochloride, and potassium cyanide is not a general one for

aromatic aldehydes, salicylaldehyde and anisaldehyde yielding only the respective aldazines. Heptaldehyde yields *heptylidenehydrazine*, $C_6H_{13} \cdot CH:N \cdot NH_2$, colourless leaflets, m. p. 133—136°, which is also obtained from aqueous hydrazine hydrate and heptaldehyde, the substance described under this name by Franzen and Eichler (A., 1910, i, 700) being really heptylideneazine.

By heating a mixture of equal molecular quantities of benzylidenehydrazine and heptaldehyde cyanohydrin on the water-bath, an oil is obtained which has the composition of benzylideneheptylideneazine, but it is probably not an individual substance, since it slowly deposits yellow crystals of benzaldazine.   C. S.

Relative Masses of Protein Anions and Cations. A. R. C. Haas (*J. Physical Chem.*, 1918, **22**, 520—524).—A repetition of the work of Robertson on the transport of casein ions by an electric current (A., 1909, i, 619; 1910, i, 526). The change in the casein concentration at the anode and cathode in the electrolysis of potassium caseinate has been determined by Robertson's method and by determination of the change in the nitrogen content at both electrodes. The results confirm those of Robertson, which show that the ratio of the loss at the anode to that at the cathode is 2. This proves that the masses of the protein anions and cations are equal, and that the current is carried in both directions by protein ions.   J. F. S.

Mucins and Mucoids. P. A. Levene and J. López-Suárez (*J. Biol. Chem.*, 1918, **36**, 105—126. Compare A., 1916, i, 681, 765).—Mucoids containing chondroitin–sulphuric acid have been obtained from the aorta and the sclera. On hydrolysis, chitosamine is produced.

Mucoitin–sulphuric acid has been obtained from funis mucin, vitreous humour, cornea, mucin of gastric mucosa, serum mucoid, ovomucoid, and ovarian cysts. On hydrolysis with hydrochloric acid, mucoitin–sulphuric acid yields *mucosin*, $C_{12}H_{21}O_{11}N,HCl$, white powder, $[\alpha]_D^{20} +25 \cdot 55°$, which is a disaccharide composed of glycuronic acid and chitosamine.   H. W. B.

Behaviour of Thymic Acid to Phenylhydrazine. R. Feulgen and G. Landmann (*Zeitsch. physiol. Chem.*, 1918, **102**, 262—265. Compare Feulgen, this vol., i, 85, 413).—Further evidence of the existence of two free aldehydic groups in thymic acid is furnished by the preparation of a diphenylhydrazone of the acid, which is isolated in the form of its barium salt. Barium thymate is dissolved in water and treated at 60° with phenylhydrazine in acetic acid solution. The temperature is then raised to 100°, and the heating continued for twenty minutes. Barium acetate is now added, and then three volumes of boiling alcohol. After cooling, the precipitated phenylhydrazone is purified by reprecipitation by alcohol from its solution in dilute acetic acid. *Barium phenylhydrazinothymate*, $C_{45}H_{53}O_{24}N_9P_4Ba_2$, is a yellow,

amorphous substance which readily decomposes when heated or treated with strong acids. Crystalline derivatives have not been obtained.   H. W. B.

Influence of certain Salts on Enzyme Action. I. S. FALK (*J. Biol. Chem.*, 1918, **36**, 229—247).—Sodium chloride accelerates slightly the rate of lipolysis of olive oil by lipase, whilst calcium chloride always inhibits it. The former does not alter the point of equilibrium of the reaction mixture; when calcium chloride is present, equilibrium is reached very much earlier than in its absence, and the higher the concentration, the greater the influence on the lipase. The addition of sodium chloride tends to prevent the appearance of the calcium effect.   H. W. B.

Peroxydases. RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1918, **416**, 21—64).—The authors have set themselves the task of so improving the methods for isolating and purifying enzymes that the following questions may be answered: (1) whether enzymic activity is possessed by an analytically pure compound or whether an "enzyme" is a system of co-operating substances, (2) whether a metal is an integral part of an enzyme, and, eventually, (3) what atomic groupings are associated with enzyme activity. As a preliminary study, the case of horse-radish peroxydase has been chosen.

For the isolation of highly concentrated peroxydase preparations, the following scheme is recommended: (I) Thin slices of the roots (5 kilos.) are kept for a few days in flowing water in order to remove the simpler products by dialysis through the cell walls. (II) The washed material is then digested with oxalic acid solution (40 grams to 10 litres) for a few hours. By this means, the regulating influence of the living protoplasm is removed, the peroxydase is precipitated, apparently adsorbed on coagulated protein material, and dialysis proceeds further, mustard oil being extracted in large quantities. So extensive is the dialysis, that the dried slices lose more than 25% in weight and half of their mineral matter. (III) The material is next crushed in a mill, washed on a filter with about 15 litres of water containing 1·5 grams of oxalic acid, and then thoroughly pressed free from sap. The residue (1·5 kilos.) is intimately triturated with baryta water, almost sufficient to overcome its acidity, then pressed again, and now treated with further quantities of baryta water to liberate the enzyme. Most of the barium is retained by the fibres, but the expressed liquid is just acidified by means of carbon dioxide to remove the remainder, and then the filtrate is mixed with nine-tenths of its volume of alcohol. Slimy substances are precipitated, and the filtrate is evaporated to 50—70 c.c. in a vacuum, from a bath at 50°. The residue is filtered again and then mixed with five times its bulk of alcohol, whereby the crude enzyme is precipitated. This is purified a little more by redissolving it in water containing a trace of sulphuric acid and reprecipitating it by

alcohol. (IV) The crude material is found to be a mixture of the enzyme with a nitrogenous glucoside, which can be precipitated as a compound with mercuric chloride. Accordingly, an aqueous solution is treated with 0·5% mercuric chloride and a trace of calcium chloride to coagulate the jelly-like double compound, the mass is filtered, and the enzyme reprecipitated by alcohol from the filtrate. The peroxydase is then dissolved in water, whereby some of the mercuric chloride compound remains undissolved, the clear solution obtained by centrifuging is reprecipitated by alcohol, and the process repeated until the enzyme dissolves clearly in water. The best preparation obtained so far amounted to 0·45 gram from 5 kilos. of horse-radish, this representing about 60% of the enzyme originally present. The glucoside compound is decomposed by $2N$-hydrochloric acid, and the glucoside obtained by precipitating the solution with alcohol amounts to about 3·4 grams.

In order to control the above operations, a method for estimating peroxydase was developed. It depends on the production of purpurogallin from pyrogallol and hydrogen peroxide, but is free from certain errors which are present in Bach and Chodat's method (A., 1904, i, 542). It is found, namely, that peroxydase is not only spoilt by too great a concentration of hydrogen ions, but by too concentrated hydrogen peroxide, and it is only fair, therefore, in devising an analytical method, to choose conditions under which the enzyme is not impaired. The method proposed is as follows. A solution of 5 grams of purest pyrogallol in 2 litres of water is mixed with about 10 c.c. of 5% hydrogen peroxide containing exactly 50 mg. of H_2O_2, regulated to 20° in a thermostat, and then treated with 1—5 c.c. of a solution of 5 mg. of the enzyme in 100—500 c.c. of water (that is, from about 0·25 mg. of the crude preparations to 0·02 mg. of the best preparation). After exactly five minutes, the action is stopped by adding 50 c.c. of dilute sulphuric acid, the purpurogallin is extracted with ether and estimated colorimetrically by comparison with a solution containing 100 mg. of the pure pigment in 1 litre of ether. The results are then translated into the number of mg. of purpurogallin which would be produced by 1 mg. of the vacuum-dried preparation. This is called the "purpurogallin number." For example, the number for the well-pounded horse-radish is about 0·25, for the crude preparation before treatment with mercuric chloride about 360, and for the best specimen yet obtained about 670. In a solution of carbon dioxide, the enzyme is not impaired, but produces only about half as much purpurogallin as in pure water. It appears as though the particular grouping in the enzyme at which hydrogen peroxide may be attached is also capable of uniting with acids. Solutions of the preparations which have not been purified by mercuric chloride become somewhat more active after a few hours, but the solutions of the purified enzyme deteriorate. Consequently, any comparisons of activity are made immediately after dissolving the preparations.

The yield of purpurogallin obtainable from pyrogallol has often

been discussed. For example, Nierenstein and Spiers (A., 1913, i, 1367) obtained 10—16%. If the pyrogallol solution is concentrated, the amount of peroxydase employed is large, and the hydrogen peroxide is added very slowly, so that it is always present in very low concentrations, the yield may be as high as 80%.

Some reactions and analytical data concerning the purest enzyme and its companion glucoside are also recorded. The enzyme appears to consist chiefly of a nitrogenous glucoside, containing a pentose (above 30%) and an equimolecular quantity of another sugar, probably a hexose. It does not seem to be very complex, and if it contains only the residues of two sugar molecules, its molecular weight would be about 500 and number of nitrogen atoms 3. It also contains about 5·5% of mineral ash, consisting of alkaline earths and iron. The amount of the latter is very small (0·46% in the best preparation), but it rises with the purification of the enzyme. It is unlikely, however, that iron plays any stoicheiometrical part in the production of purpurogallin, for it may be calculated that the activity of the best preparation would mean a consumption of 297—355 molecules of hydrogen peroxide in one second for every atom of iron present. Furthermore, the addition of ferrous salts is of no influence in the reaction. The companion nitrogenous glucoside, which is precipitated by mercuric chloride, is a high molecular compound. Its vapours give the pyrrole reaction, and it also gives the Millon and xanthoproteic reactions. It contains about 50% of pentose residues, and a hexose, and the proportion of nitrogen is about 3 atoms to every 2 pentose molecules.

Oxyhæmoglobin has often been compared with peroxydase, and Wolff and de Stoecklin have even stated that they do not differ in peroxidative action (A., 1910, i, 802). This is chiefly because rich peroxydase preparations had not been employed hitherto, for oxyhæmoglobin is only about one-thousandth part as active as a quantity of peroxydase containing the same amount of iron. Iron compounds, such as the tannate or a ferrocyanide (Wolff, A., 1911, ii, 795) or sulphate, are also very feeble in their activity compared with peroxydase.   J. C. W.

Physiological Chemistry.

Distribution of Phosphoric Acid in Normal Human Blood. W. R. BLOOR (*J. Biol. Chem.*, 1918, **36**, 49—57).— There are two classes of phosphoric acid compounds in human blood, (1) those soluble in dilute acids and precipitated by alcohol–ether, (2) those soluble in alcohol–ether and precipitated by dilute acids. The sum of these two groups is, in general, equal to the total phosphates, so that the presence of other forms of combina-

tion of the phosphoric acid in blood, in significant amounts, is improbable.

The second group contains substances of the type of lecithin; the first group comprises the inorganic phosphates and an unknown compound, which is decomposed by heating with acids, yielding phosphoric acid. The amount of the unknown compound in plasma is about 10% of the total phosphates, whilst in the corpuscles it ranges between 60% to 80% of the total phosphates. The possible significance of this compound is discussed.   H. W. B.

Phenols and Phenol Derivatives in Human Blood in some Pathological Conditions. RUTH C. THEIS and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **36**, 99—103).—By means of the method previously described (this vol., ii, 461), it is found that the amount of phenols in pathological blood may vary between 1·87 and 7·96 mg. per 100 c.c. of blood.   H. W. B.

The Pigments of Blood Serum. G. PATEIN (*J. Pharm. Chim.*, 1918, [vii], **18**, 225—238).—From a series of tests, the author concludes that Fouchet's method (compare this vol., ii, 415) for the detection of biliary pigments in serum is not vitiated by the presence of indoxyl. The methods of Troisier and Berthelot (compare *Compt. rend. Soc. Biol.*, 1912, 259) and of Giraud and Montpellier (compare *Bull. Soc. chim.*, 1917, 132) for the detection of indoxyl give good results. If the amount of indoxyl present is small, it is better to extract it from the serum with alcohol and examine the residue left after evaporating the alcohol. The addition of a trace of ferric chloride to the hydrochloric acid makes the reaction more sensitive.

A new blue pigment has been discovered in blood serum which does not form under the oxidising action of reagents. It is characterised by its solubility in 0·6% sodium chloride solution and its insolubility in the solvents which dissolve the other pigments. It is much less stable than either bilicyanin or indigotin. At present it is only possible to state that it is a complex formed by a blue substance and globulin. It has been found in most of the serums examined, but in very small amounts.   W. G.

Concentration of Antitoxic Sera by the Salting Out of the Heat-denaturated Serum Proteins with Sodium Chloride. ANNIE HOMER (*Biochem. J.*, 1918, **12**, 190—209).— The concentration of antitoxic sera can be successfully conducted by a regulation of the heat-denaturation of the serum proteins, followed by a direct treatment of the heated sera with brine and salt. The end-products thus obtained are clear and readily filterable, as they do not contain the colloidal suspension of heat-denaturated protein which is so often found in those resulting from methods involving the use of ammonium sulphate. The new method does not effect the removal of as great a proportion of the serum proteins as the Banzhaf and Homer methods (this vol.,

i, 138), and the degree of concentration of antitoxin in the end-product is also lower than can be obtained by the former methods.

H. W. B.

Uric Acid Metabolism. I. The Influence of High Protein Diets on the Elimination of Endogenous Uric Acid. HOWARD B. LEWIS and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 1—7).—No difference is observed in the amount of uric acid excreted by two men maintained for successive periods on purine-free high protein diets containing (*a*) much arginine and histidine, and (*b*) little of these amino-acids. This result does not appear to be in harmony with the conclusions drawn by Ackroyd and Hopkins (A., 1917, i, 237) from their experiments, namely, that arginine and histidine constitute the raw material for the synthesis of the purine ring in the animal body. H. W. B.

Uric Acid Metabolism. II. Proteins and Amino-acids as Factors in the Stimulation of Endogenous Uric Acid Metabolism. HOWARD B. LEWIS, MAX S. DUNN, and EDWARD A. DOISY (*J. Biol. Chem.*, 1918, **36**, 9—26. Compare this vol., i, 277).—A full account of work previously published.

H. W. B.

Rôle of Inorganic Sulphates in Nutrition. AMY L. DANIELS and JEAN K. RICH (*J. Biol. Chem.*, 1918, **36**, 27—32). —The addition of inorganic sulphates to the diet of young rats does not increase the rate of growth, even when the diet is deficient in cystine. These animals are apparently unable to synthesise cystine from inorganic sulphates. H. W. B.

Biochemical Mechanism of Growth. The Effect of Sodium and Calcium Ions on the Growth of a Transplantable Mouse Carcinoma. WILLIAM CRAMER (*Biochem. J.*, 1918, **12**, 210—220).—When the cells of a transplantable mouse carcinoma are placed in an isosmotic solution of calcium chloride, they lose water, and on subsequent transplantation show a much slower rate of growth than is exhibited by similar cells transplanted without any such treatment. Both the inhibition of growth and the loss of water produced by calcium ions can be antagonised by a subsequent suspension of the cells in sodium chloride solution. This inhibition of growth produced experimentally, and the subsequent recovery from it, present a similarity to the spontaneous fluctuations in growth which are exhibited normally by tumour cells in the course of their propagation. The bearing of these results on the question of the possibility of the discovery of a cure for cancer is discussed. H. W. B.

Rôle of the Liver in Hippuric Acid Synthesis. E. LACKNER, A. LEVINSON, and WITHROW MORSE (*Biochem. J.*, 1918, **12**, 184—189).—The injection into dogs of hydrazine sulphate,

which poisons the liver without interfering with the functions of the kidney, appears to inhibit the subsequent formation of hippuric acid from administered sodium benzoate. In dogs, therefore, as in rabbits, the liver seems to participate in the synthesis of hippuric acid (compare Kingsbury and Bell, A., 1915, i, 739).   H. W. B.

Thyroid Hormone and its Relation to the other Ductless Glands. E. C. KENDALL (*Endocrinology*, 1918, **2**, 81—93. Compare A., 1917, i, 364).—The name *thyroxin* (from thyro-oxy-indole) is suggested for the active principle of the thyroid gland. It has the constitution I. In the alkaline body fluids it

(I.)   (II.)
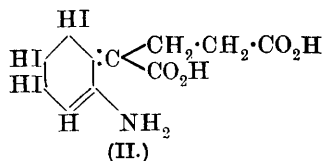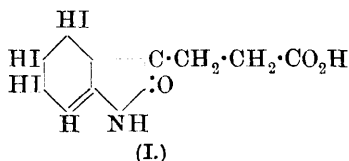
is considered to occur in the hydrated condition (II). An adult has a total amount of 23—50 mg. A dose of $\frac{1}{3}$ mg. increases the basal metabolic rate by 1%, or a dose of 10 mg. by 30%. The synthesis of a small quantity is stated to have been effected by the author's collaborator, Osterberg.   G. B.

Arginase. V. Presence of Arginase in the Organism of certain Invertebrates. A. CLEMENTI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 299—302).—The author's previous results render it of interest to ascertain if arginase exists in the organism of invertebrates, and if in the latter any relation is detectable between arginase and the type of the nitrogenous exchange. The work now described shows that this enzyme is absent from the aqueous extracts of the hepato-pancreas of *Astacus fluviatilis* and of the larvæ of thermites, but that it is present in the hepato-pancreas of *Helix pomatia*.   T. H. P.

Hydrolysis of the Cocoon-silk of the Bivoltine Species "Daiwanishiki" (the Authum Breed), and of Sericine separated from the same Silk. RYŪGO INOYE and KATSU HIRASAWA (*J. Tokyo Chem. Soc.*, 1918, **39**, 300—320).—Cocoon silk, cultivated in the Ueda College of Sericulture in middle Japan. was hydrolysed, and the following percentages of amino-acids, calculated on the dry silk, were obtained by the ester method: glycine 25·42, alanine 22·58, leucine 0·62, aspartic acid 0·11, glutamic acid trace, proline 0·32, serine 2·77, phenylalanine 0·25, and tyrosine 5·68. The cocoon silk contained 24·2% of sericine, and this on hydrolysis yielded: glycine 3·86%, alanine 3·47%, leucine 0·39%, aspartic acid 3·91%, glutamic acid 0·81%, proline 0·35%, serine 5·89%, phenylalanine 0·49%, and tyrosine 3·18%.

The author draws the conclusion that the amino-acids contained in the silk of the bivoltine species seem to be quite similar in

amount and nature to those of the monovoltine species, but the sericine separated from the silk of the bivoltine species has a chemical constitution somewhat different from that of the monovoltine species, which have been investigated previously; that there is a difference is in agreement with the fact that the cocoons of the former species can be more easily reeled than those of the latter.

S. H.

Cholesterol in Milk. W. Denis and A. S. Minot (*J. Biol. Chem.*, 1918, **36**, 59—61).—Cow's milk contains from 10 to 18 mg. of cholesterol per 100 c.c. of milk. The corresponding figures for human milk range between 10 and 40. The amount of cholesterol in the milk appears to be determined by the amount in the food.

H. W. B.

Detection, Estimation, and Elimination of Arsenic and Mercury in Urine. Paul Duret (*Compt. rend. Soc. Biol.*, 1918, **81**, 736—737, 737—739).—In both cases, organic matter is destroyed by ammonium persulphate in sulphuric acid solution (compare this vol., ii, 335). Arsenic is estimated by converting it into arsenic trihydride and passing into silver nitrate; the reduced silver is estimated with potassium cyanide. Mercury is precipitated with ammonia, converted into the hydrochloride, and tested qualitatively in ethereal solution with diphenylcarbazide (blue coloration), and estimated with standard solutions of potassium cyanide and silver nitrate. After "novarsenobenzol" (neo-salvarsan), arsenic appears in the urine in the first twenty-four hours, and may persist for twenty days. The greatest amount eliminated was 12 mg. of arsenic in twenty-four hours after a dose of 900 mg. novarsenobenzol containing 190 mg. of metallic arsenic. The elimination is most rapid in the first forty-eight hours, and generally falls after four days to 1 mg. per twenty-four hours. Ten mg. per twenty-four hours is about the maximum with which the kidneys can deal. In a course of four injections at intervals of a week, scarcely one-fifth of the arsenic is eliminated.

Mercury appears in the urine in small quantities in the first twenty-four hours after injection.

G. B.

Creatine Excretion in Ruminants. John Boyd Orr (*Biochem. J.*, 1918, **12**, 221—230).—The amount of creatine excreted by a goat or a sheep is relatively large, and is inversely proportional to the amount of carbohydrate in the diet. Cessation of lactation causes a decrease in the amount of creatine excreted. The author advocates the view that creatine is formed in relatively large quantities from a substance other than protein and that its utilisation is intimately connected with the metabolism of carbohydrate.

H. W. B.

Vitamine Studies. I. The Catalase Activity of the Tissues in Avian Polyneuritis. R. Adams Dutcher [with Ferdinand A. Collatz] (*J. Biol. Chem.*, 1918, **36**, 63—72).—The

catalase content of the tissues is lowered to the extent of 44% in avian polyneuritis. With the recovery from polyneuritis through the administration of vitamines (water-soluble B), there is a corresponding rise in the amount of catalase in the tissues until the normal figures are reached. Polyneuritis is accompanied, therefore, by incomplete oxidation, and consequently there is an accumulation of toxic products in the tissues. It is the function of the water-soluble vitamine to stimulate, directly or indirectly, the oxidative processes, and thereby effect the removal of these toxic compounds. In pigeon tissues, the content of catalase (as measured by the oxygen liberated from hydrogen peroxide), the metabolic activity and the content of water-soluble vitamine appear to stand in direct relation to one another.   H. W. B.

Preparation of Antineuritic Substances from Carrots and Yeast. KANEMATSU SUGIURA (*J. Biol. Chem.*, 1918, **36**, 191—196).—Aqueous and alcoholic extracts of carrots and of yeast cure polyneuritis in pigeons. A colourless, crystalline substance capable of exerting a curative action on polyneuritic pigeons can be prepared from dried, powdered brewer's yeast by treating it with ten times its weight of 5% sodium chloride solution, and, after placing in a collodion bag, subjecting it to air dialysis (Kober, A., 1917, ii, 295). By this method, 22 mg. of colourless, crystalline substance, almost free from sodium chloride, can be obtained from 10 grams of dried yeast. A solution in water of from 2 to 5 mg. of these colourless crystals injected subcutaneously into a pigeon may be sufficient to abolish completely the symptoms of polyneuritis within a few hours. The crystals are not very soluble in water, and the solution gives a deep blue colour with Folin's phosphomolybdic–phosphotungstic reagent for the detection of phenolic substances.   H. W. B.

Antiscorbutic Factor in Lemon Juice. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 259—269). —The free citric and other organic acids in lemon juice may be removed by precipitation with calcium carbonate without impairing the antiscorbutic power of the juice. If, after acidifying, the filtered lemon juice is evaporated in a vacuum at 30—40°, an active, dry residue is obtained which, when administered to guinea-pigs on an otherwise scorbutic diet, prevents the onset of scurvy. The treated lemon juice had a curative effect when given to a scorbutic monkey, but it did not seem to arrest the progress of well-marked scurvy in guinea-pigs when administered by subcutaneous injections. The administration of very concentrated doses of treated lemon juice previous to depriving guinea-pigs of the antiscorbutic factor does not prevent or delay the onset of scurvy.   H. W. B.

Etiology of Scurvy in Guinea-pigs. ARTHUR HARDEN and SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1918, **12**, 270—274).— The fact that all the citrates can be removed from lemon juice

without impairing its antiscorbutic qualities (see preceding abstract) indicates that the antiscorbutic power of orange juice cannot be due to the laxative action of its constituent citrates, as contended by McCollum and Pitz (A., 1917, i, 604). Experiments are now described which prove that lactose and other carbohydrates do not possess the slightest antiscorbutic power, and the contrary results obtained by Pitz (*J. Biol. Chem.*, 1918, **33**, 471) are shown to be due to the considerable amounts of fresh milk (compare Chick, Hume, and Skelton, this vol., i, 360) instead of the carbohydrates in the diets employed by that worker. The authors draw the conclusion that scurvy in the guinea-pig does not arise through the absorption of toxins consequent to constipation in the intestine, but is due to the deficiency of a necessary accessory factor in the diet. H. W. B.

Genesis of Thiocyanic Acid in Animals. III. SERAFINO DEZANI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 189—207; from *Physiol. Abstr.*, 1918, **3**, 309. Compare this vol., i, 360).—After giving acetonitrile to dogs in toxic doses, hydrocyanic acid appeared in the urine. This transformation could not be brought about by organ (liver) infusions. Neither hydrocyanic nor thiocyanic acid was excreted after ingestion of purines and amino-acids.
H. W. B.

Pharmacology of the Hydroxyhydroaromatic Compounds. Y. SASAKI and K. OKUSHIMA (*Acta Schol. Med. Kyoto*, 1918, **2**, 257—270; from *Physiol. Abstr.*, 1918, **3**, 335. Compare Sasaki, A., 1917, i, 677).—The toxicity of these compounds towards frogs, as towards mammals (*loc. cit.*), diminishes as the number of hydroxyl radicles increases. When, however, the effects on separate organs are ascertained, some departures from the main generalisation are found. Paralysis of motor nerve-endings occurs only with *cyclo*hexanol and *i*-inositol. *cyclo*Hexanol exerts a paralysing action on muscle, whilst *i*-inositol shows first excitation and later paralysis. Phloroglucinol produces only excitatory effects on the heart; *i*-inositol causes slowing and irregularity of cardiac contractions, whilst *cyclo*hexanol causes weakening of systole.
H. W. B.

Pharmacology of the Vitamines. II. FR. UHLMANN (*Zeitsch. Biol.*, 1918, **68**, 457—498. Compare this vol., i, 419).— The action of vitamine preparations from various sources (orypan, extracts of oats, nettles, blood, etc.) on animal tissues is closely paralleled by the actions of pilocarpine and choline. The intestinal muscles are caused to contract, the action of the heart is depressed, the blood pressure is lowered, and the blood vessels dilated exactly as occurs when the respective tissues are treated with pilocarpine. Moreover, the action of the vitamine, like that of pilocarpine or choline, is antagonised by atropine. The conclusion previously drawn by the author is therefore confirmed,

namely, that the antineuritic vitamine is a substance physiologic-
ally closely related to pilocarpine, which acts on the sympathetic
nerve-endings and thus exerts a controlling influence on the tonus
of the muscles in the organism.   H. W. B.

Chemistry of Vegetable Physiology and Agriculture.

Antiseptic Properties of certain Organic Compounds.
I. J. KLIGLER (*Proc. Soc. Amer. Bacteriologists, Abstr. Bacteriol.*, 1918, **2**, 19; from *Physiol. Abstr.*, 1918, **3**, 350. Compare this vol., i, 469).—The composition and the degree of acidity of the medium exert a marked influence on the antiseptic properties of aniline and its derivatives. The higher the concentrations of organic nitrogenous compounds in the medium, the lower is the effective concentration of the antiseptic.   H. W. B.

Theory and Practice of Disinfection by Alcohol. JOHANNE CHRISTIANSEN (*Zeitsch. physiol. Chem.*, 1918, **102**, 275—305).—The disinfecting power of an alcohol depends not only on its ability to precipitate the proteins of bacteria, but on its capacity to penetrate the cell walls, and thus exert its action on the protoplasm of the bacteria. The latter quality is dependent on the surface tension of the alcohol. Propyl alcohol seems to be the most suitable of all the alcohols for direct application to the skin as a means of disinfection prior to surgical operation. Its toxicity is considerably greater than that of ethyl alcohol, and on account of its dissolving power over fats, it is able to enter readily the pores of the skin.   H. W. B.

Yeast Growth. ARTHUR SLATOR (*Biochem. J.*, 1918, **12**, 248—258).—The author describes a method of measuring rates of growth of yeast cells by direct observation under the microscope.

When old yeast cells are introduced into a fresh medium, they remain quiescent for some time (lag). They then start growing at the normal unrestricted rate, and subsequent growth proceeds normally in alternate periods of rest and growth. Carbon dioxide retards growth. Air (oxygen) is essential for yeast growth; oxygen, chemically combined in the medium, as well as dissolved oxygen, may be utilised by the yeast. [See, further, *J. Soc. Chem. Ind.*, 746A.]   H. W. B.

General and Physical Chemistry.

Optical Researches on the Constitution of Bismuth Compounds. KONR. SCHÄFER and FR. HEIN (*Zeitsch. anorg. Chem.*, 1917, **100**, 249—303).—Optical differences between ions and undissociated molecules may be due to a change in the composition of the chromophore through dissociation, or more probably to the fact that the absorption spectrum is dependent on the degree of solvation of the chromophoric cation. The dissociation of a salt KA with a coloured cation may be represented by the scheme:

$$KA \longrightarrow \left[\begin{matrix} A \\ K(OH_2)_n \end{matrix} \right] \longrightarrow [K(OH_2)_n]A \longrightarrow [K(OH_2)_n]^{\cdot} + A'.$$
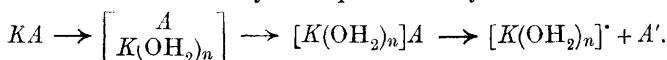
The degree of completion of dissociation at any dilution depends on the relative strengths of the affinities $K \longleftrightarrow A$ and $K \longleftrightarrow$ solvent, and the solution may come to a condition of optical equilibrium before complete dissociation. If the force $K \longleftrightarrow A$ is strong, dissociation is incomplete and the anion remains combined with the chromophoric complex. This condition of affairs probably obtains in the case of the bismuth haloids.

Solutions of bismuth chloride in aqueous hydrochloric acid show a deep absorption band having its apex at $1/\lambda = 3070$. Since the depth and persistence of the band are both increased by increasing the concentration of the acid, it is probable that there is formed in solution a complex bismuthchlorhydric acid. In weaker acid solutions, although the depth of the absorption band is less than with stronger acid, the intensity in the neighbourhood of the band minimum is much greater. This is taken as evidence of the forma-

tion of bismuthyl complexes in such solutions. Proof of this is furnished by the observation that weakly acid solutions of bismuth chloride in equilibrium with solid bismuth oxychloride show an even greater intensity at the minimum point with an increase in the width of the band. The absorption curves of bismuth chloride in ammonium chloride solutions are practically the same as in hydrochloric acid solutions.

Solutions of bismuth chloride in dry ether or ethyl acetate give probably the true absorption band of the salt itself. The band is farther in the ultra-violet than in hydrochloric acid solutions, having its maximum near $1/\lambda = 3400$, and is shallower. Addition of hydrochloric acid and a very small quantity of water to the ethereal solution, however, shifts the band back to the same position as in the aqueous acid solutions. The remarkable effect of the water makes it seem probable that the absorbing complexes are of the type

$$\left[BiCl_2 \frac{Cl}{(OH)_2} \right] H \quad or \quad \left[BiCl_2 \frac{Cl_2}{OH_2} \right] H_2.$$
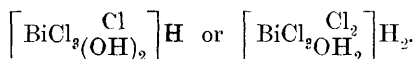
By leading dry hydrogen chloride into an ethereal solution of bismuth chloride, a new compound, $BiCl_3, HCl, 2OEt_2$, was isolated, in the form of a colourless, viscous oil.

Bismuth bromide in aqueous hydrobromic acid is similar to bismuth chloride, the absorption band being shifted into the visible spectrum with its maximum near $1/\lambda = 2700$. In ether, the band is shifted towards the violet, and there is only a suggestion of selective absorption. Addition of hydrogen bromide to the ether solution, however, immediately brings the band back to $1/\lambda = 2700$, without the addition of water. The inference is that the absorbing complex is a simple bismuthbromhydric acid.

Two new compounds of bismuth bromide were isolated in the form of unstable hygroscopic powders, their compositions being $H_2BiBr_5, 4OEt_2$ and $H_2BiBr_5, 10OEt_2$.

Bismuthyl compounds, such as potassium tribismuthyl tartrate and compounds with glycerol and mannitol, show only general absorption in the region of the bismuth chloride band in ether. Bismuth nitrate, sulphate, and perchlorate in aqueous solutions of their respective acids show slight general absorption in the ultra-violet. The conclusion is drawn that, since bismuth ions and bismuthyl compounds show no absorption bands, the bismuth haloids must be classed with abnormal salts of the type of mercuric cyanide.

Bismuth trimethyl in alcohol, bismuth triphenyl in ether, and bismuth triphenyl dichloride in chloroform all show fairly strong general absorption in the ultra-violet. For the preparation of bismuth trimethyl, a new method was devised, using Grignard's reagent.   E. H. R.

The Influence of Solvents on the Absorption of Light by Dissolved Substances. A. HANTZSCH (*Ber.*, 1917, **50**, 1413—1421). —From earlier investigations, it is probable that the accuracy of

the optical absorption method for the examination of keto-enol
equilibria with ethyl acetoacetate and similar substances is not
seriously influenced by the formation of additive compounds
between solute and solvent.   Evidence to this effect is also supplied
by the behaviour of the structurally simple trinitrotriphenylcarbinol,
which exhibits almost identical absorption curves in methyl alcohol
and in chloroform, although with these substances it forms isolable
additive compounds, $OH \cdot C(C_6H_4 \cdot NO_2)_3, CH_3OH$ and
$$OH \cdot C(C_6H_4 \cdot NO_2)_3, CHCl_3$$
respectively.   The character of the absorption by trinitrotriphenyl-
carbinol, and presumably by all substances of definite and fixed
constitution, is therefore not appreciably affected by combination
with the solvent.   The fact that acetic acid in the pure condition
and in concentrated aqueous solution possesses identical absorptive
properties for light (Hantzsch, A., 1914, ii, 5) proves that mere
hydration also is without optical effect, and even association into
the bimolecular condition, as experienced with acetic acid and
with trichloroacetic acid, has no marked influence in this direction;
a parallelism is suggested between the formation of such unstable
molecular compounds in which the combined molecules are alike
and unlike, the processes being described respectively as homo-
geneous and heterogeneous association.   Heterogeneous association
with an optically transparent medium is generally accompanied by
a slight change in the absorption curve of the solute, but the
general nature of the absorption remains unaltered.   As very few
substances can be regarded as completely saturated, slight changes
in the absorption spectrum may be met frequently.   In contrast
with such cases stands the behaviour of substances which in
different solvents show essentially diverse absorption, due to definite
constitutional modification, the extent of which is influenced by
the solvent; tautomeric substances present the best known examples
of this class.   In considerations such as these, care is necessary to
avoid confusion with cases in which chemical reaction occurs
between solvent and solute, with the formation of new substances
possessing absorptive properties different from those of the solute;
the medium is then better described as a pseudo-solvent.   Chloral
and alloxan dissolved in water undergo loss of the ketonic oxygen
with replacement by two hydroxyl groups, and this definite struc-
tural change produces a corresponding marked alteration in the
absorption spectrum of each.   From the point of view now under
consideration, genuine solvents either give rise to no marked
"solvate" formation or form unstable and feeble heterogeneous
association products involving only trivial chemical and optical
alteration; they may, however, by affecting the stability of the
solvates, influence the equilibrium between the stable and meta-
stable forms of a tautomeric substance, and thereby produce
material alteration in the chemical constitution and optical
properties.   It is necessary to remember the possibility that a
liquid may act concurrently in two different ways, partly as a
genuine solvent and partly as a pseudo-solvent with chemical

1—2

action, thus giving rise to an equilibrium between solvates and chemical compounds.   D. F. T.

The Constitution of Carboxylic Acids and the Optical and Chemical Processes in the Formation of Esters, Salts, and Ions.

A. HANTZSCH (*Ber.*, 1917, **50**, 1422—1457. Compare preceding abstract).—The ordinary structural formula $R \cdot CO \cdot OH$ for the carboxylic acids is insufficient for many purposes, and fails, for example, to explain satisfactorily the relative ease with which the hydrogen of the hydroxyl group undergoes scission by electrolytic dissociation. The optical absorptive characteristics of the organic acids and their derivatives also demand an improved method for formulating the structure of the acids; thus the salts of a fatty acid with the alkali or alkaline earth metals are optically identical with one another, as also are the alkyl esters, but the esters always exhibit a more marked absorption than the salts, whilst the free acids commonly occupy an intermediate position, although in extreme cases they may become optically identical with the salts or with the esters; these optical differences can be due only to chemical, and therefore to constitutive, differences, because chemically and optically indifferent solvents have only a negligible effect on the absorption spectrum of the solute (see preceding abstract), association of a fatty acid, for example, acetic acid, does not affect the absorption, electrolytic dissociation is without influence on the optical absorption by fatty acids, and the mere replacement of the hydrogen of an acid by an alkyl radicle leaves the absorption spectrum practically unchanged. Investigation of trichloroacetic acid demonstrates that in solution in water or light petroleum the acid possesses optical properties coincident with those of aqueous solutions of the salts, but that in alcohol or ether the absorption by the acid is identical with that of solutions of the esters in alcohol, ether, or light petroleum, the two absorption curves being quite distinct; this difference cannot be explained by assuming the formation of an acid ortho-ester in alcoholic solutions of the acid, because ortho-esters, being more saturated, should possess more feeble absorptive powers, whereas the alcoholic solutions of trichloroacetic acid give the absorption band nearer the visible spectrum. The conclusion is therefore drawn that whilst the alkyl groups in the alkyl esters are attached to an oxygen atom in the usually accepted manner, the ionisable atoms are attached to both oxygen atoms, the structure of the salts and acid being representable by the formulæ $CCl_3 \cdot C {<}^O_O \} M$

and $CCl_3 \cdot C {<}^O_O \} H$ respectively, these constitutions being analogous to Werner's method of expressing the ionisability of inorganic salts by "ionogenic" linkings; the formula $R \cdot CO \cdot OH$ therefore is that of a *pseudo*-acid corresponding with a true acid of the structure $R \cdot C {<}^O_O \} H$. Although trichloroacetic acid from its absorp-

tion spectrum appears to be of the former constitution in alcoholic or ethereal solution, and of the latter constitution in water or light petroleum, the phenomenon is in reality one of equilibrium, and by more sensitive methods of examination, for example, by means of the electrical conductivity, it is possible to detect the presence of a definite, although small, proportion of the true acid modification in the alcoholic solution. The behaviour of other carboxylic acids is of the same general character as that of trichloroacetic acid, but somewhat less simple, solutions in alcohol or ether containing the acid almost entirely in the pseudo-modification, whilst the acid in the free state or when dissolved in light petroleum or water consists of a mixture of the pseudo- and true acid modifications in equilibrium. In this case, the relation between the esters, the free acid, and the salts may be represented by the scheme: $R \cdot CO \cdot O \cdot C_nH_{2n+1}, R \cdot CO \cdot OH \rightleftharpoons R \cdot CO_2 \colon H, R \cdot CO_2 \colon M$;   the position of the equilibrium for the free acid will be dependent on the specific nature of the acid and on the character of the solvent, the latter influencing the relative stability of the two modifications by the formation of solvates; thus, with trichloroacetic acid in aqueous solution, the hydrate, $CCl_3 \cdot CO_2 \colon H, (OH_2)_n$, is stable, whereas in alcoholic solution, the alcoholate, $CCl_3 \cdot CO_2 \colon H, (C_2H_6O)_n$, is unstable and tends to change into the stable alcoholate,

$$CCl_3 \cdot CO \cdot OH, (C_2H_6O)_n$$

(compare preceding abstract). The position of equilibrium between the two modifications of a carboxylic acid will be directly connected with the strength of the acid, so that with successive replacement of the hydrogen in acetic acid by chlorine, the absorption spectrum of the product in the pure condition or in solution in light petroleum will gradually approach that of the salts; with a very strong acid such as trichloroacetic acid, the constitution under the conditions named will be exclusively of the true acid type, and the absorption will therefore be identical with that of the salts, as experiment actually shows. On account of impurities difficult to remove, the identity of the absorption curves for all salts of the same acid has occasionally not been realised, but with pure materials, the simplicity of the relations becomes evident (compare Hantzsch, A., 1913, ii, 893; 1914, ii, 5, 230). Confirmatory details are given of the results of spectrum absorption experiments and considerations with acetic acid, chloroacetic acid, and formic acid, their salts and esters, whilst in analogy with the above considerations, nitric acid is represented by the two constitutional formulæ $NO_2 \cdot OH$ and $NO_3 \colon H$, from which the esters and salts are respectively derived.

In explanation of the noteworthy fact that alcohol affects the optical properties of the salts of fatty acids in a similar manner to, but in a less degree than those of the free acids, it is suggested that whereas in aqueous solution the salts correspond with the true acid constitution, the effect of alcohol is to cause a partial transformation of the "true salts," $R \cdot CO_2 \colon M$, into "pseudo-salts" of the structure $R \cdot CO \cdot OM$; the tendency to the formation of

pseudo-salts will be greater the less positive the nature of the cation and the less negative the nature of the anion.

The suggestion is made that the simultaneous attachment of an ionisable hydrogen (or metal) atom at two oxygen atoms, which is termed the "ionogenic condition," is of greater significance than the mere presence of hydrogen ion or the occurrence of ionisation; for example, ethyl diazoacetate is extremely rapidly decomposed by trichloroacetic acid in light petroleum, whereas in alcohol the reaction is exceedingly slow, and in ethereal solution does not occur at all; the difference in behaviour is due to the difference between the true acid and pseudo-acid modifications of trichloroacetic acid, and the catalytic effect commonly attributed to hydrogen ion is in reality due to the hydrogen atom ionogenically fixed in the molecule of the true acid (see also Snethlage, A., 1915, ii, 615, 825). Mere ionisation causes no alteration in the optical absorptive properties of a substance, but this absence of alteration is characteristic also of the conversion of transparent metallic salts into aquo-salts and of the formation of hydrates and solvates; any apparent exceptions to this rule are to be attributed to chemical or structural change in the acid, as described above for the fatty acids; this also under the influence of solvate formation accounts for the frequently observed effect of solvents which otherwise might be expected to be without action on the ultra-violet absorption of the solute.   D. F. T.

The Hypothesis of the Existence of a Third Simple Radioactive Substance in the Uranium Pleiad.

A. PICCARD (*Arch. Sci. phys. nat.*, 1917, [iv], **44**, 161—164).—The hypothesis is that actinium is not derived from either uranium-*I* or uranium-*II*, but from a third isotope of uranium, called Actin-uranium (AcU), which does not belong to the uranium–radium family, but is a primary radio-element at the head of the actinium family, with atomic weight greater than that of uranium. If 238 is the atomic weight of uranium-*I* and 240 that of actinouranium, the actual atomic weight found for uranium, 238·16, would be explained, and also how it is that the atomic weight of radium and of lead, derived from uranium-*I*, are respectively exactly 226 and 206. It is considered incomprehensible and without analogy to suppose that an atom can transform itself in two different ways by emitting an α-particle, and uranium-*Y* is regarded as the product of the α-ray change of actinouranium. In the Geiger-Nuttall relation the values of the constants are the same for all members of the same family, and the difference in the constants for the radium and actinium families indicates that the actinium family is completely distinct from that of the radium family.   F. S.

Electrical Double Refraction in Binary Liquid Mixtures.

C. BERGHOLM (*Ann. Physik*, 1917, [iv], **53**, 169—176).—The variation of the electric double refraction of binary mixtures with the composition has been examined in the case of mixtures of carbon disulphide and *m*-xylene, carbon disulphide and carbon tetra-

chloride, chlorobenzene and carbon tetrachloride, chlorobenzene and *m*-xylene, and also carbon disulphide and chloroform. The data obtained for the first pair of liquids agree with the values calculated from the mixture rule, but this does not express the behaviour of the remaining pairs of liquids.   H. M. D.

Influence of Pressure on the Electrical Conductivity of Pure Metals according to E. Grüneisen's Theory. II.

BENGT BECKMAN (*Physikal. Zeitsch.*, 1917, **18**, 507—509. Compare A., 1915, ii, 134).—The influence of pressure on the electrical conductivity of thallium, tantalum, molybdenum, and tungsten has been measured for pressures varying from 700 to 2000 atmospheres. The pressure-coefficient found by experiment is in all cases greater than the value derived from Grüneisen's theory.   H. M. D.

Transmission of a Detonation in Liquid Explosives.

R. BECKER (*Zeitsch. Elektrochem.*, 1917, **23**, 304—308).—A theoretical paper, in which the elevation of temperature produced in ethyl ether (i) by adiabatic compression, and (ii) by a compression wave, is deduced. The value is calculated by formulæ which are derived in the paper for pressures between 100 and 100,000 atmospheres. The following values of $(T_2 - T_1)$ are obtained (i) for adiabatic compression: 100 atms., $1\cdot6^\circ$; 1000 atms., $15\cdot6^\circ$; 10,000 atms., 85°; and 100,000 atms., 245°; (ii) for a compression wave: 100 atms., $1\cdot6^\circ$; 1000 atms., $15\cdot6^\circ$; 10,000 atms., 113°; and 100,000 atms., 975°. These calculations are made on the basis that C_p is constant and that the Tammann equation of condition is valid. As a result of the calculations, it is suggested that the detonation of glyceryl nitrate is to be explained by the rise of temperature which accompanies the enormous increase of pressure.   J. F. S.

Molecular Attraction. XV. Specific Heats of the Elements and some Energy Changes. II.

J. E. MILLS (*J. Physical Chem.*, 1917, **21**, 623—643. Compare A., 1917, ii, 356).—The atomic heat curves of a number of elements are compared, and it is shown that if the total energy required to raise a monatomic element from absolute zero and transform it into liquid at the melting point is divided by the absolute melting temperature a number is obtained which is nearly the same as the specific heat of the liquid element at its melting point. The energy contents of liquid elements at their respective melting points are approximately proportional to the absolute melting temperatures. The values fall between $7\cdot5T$ and $8\cdot5T$ calories per gram atom.

On the assumption that the attractive forces between molecules operate in accordance with the inverse square law, it is possible to calculate the energy contents of the liquid elements at their melting points, the results so obtained being generally in good agreement with the values derived from the atomic heat curves and the latent heats of fusion.   H. M. D.

Isothermals of Diatomic Substances and their Binary Mixtures. XIX. A Preliminary Determination of the Critical Point of Hydrogen. H. KAMERLINGH ONNES, C. A. CROMMELIN, and P. G. CATH (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 178—184).—The development of the hydrogen vapour thermostat for the maintenance of low temperatures within $\pm 0.01°$ has enabled the authors to determine the critical temperature and pressure of hydrogen. The values recorded are $T_c = 33.18°$ (abs.) and $p_c = 12.80$ atm.

The equation of the rectilinear diameter is $y = + 0.04416 - 0.000398T$, which gives $d_c = 0.0310$ for the critical density.

H. M. D.

The Critical Temperature and Pressure of Mercury and Phosphorus. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1917, **20**, 138—148).—In the light of the measurements of the vapour pressures of mercury recorded by Cailletet, Colardeau, and Rivière, the author has recalculated the critical data, the values obtained being $T_c = 1172°$ (absolute), $p_c = 180$ atmospheres, and $d_c = 3.3$. The values of $b_c = 149 \times 10^{-5}$ and of $\sqrt{a_c} = 10.74 \times 10^{-2}$ are also recorded.

The fact that a much higher critical temperature (1260°) was obtained in a previous paper (A., 1916, ii, 610) is attributed to anomalies in the behaviour of mercury at temperatures below 500°.

The available data for the vapour pressure of liquid phosphorus lead to $T_c = 948°$ (absolute) and $p_c = 80$ atmospheres.   H. M. D.

Physical Behaviour and Molecular Properties of Liquids. W. HERZ (*Zeitsch. Elektrochem.*, 1917, **23**, 301).—In previous papers (A., 1915, ii, 682, 823; 1917, ii, 194) the author has shown that the solubility of organic liquids is dependent on the molecular diameter, and that the molecular diameter increases regularly with the number of carbon atoms in the molecule. In the present paper the author continues his theoretical researches. It is shown that the latent heat of vaporisation in homologous series decreases with increasing number of carbon atoms in the molecule and also with increasing molecular diameter. It is also shown that the dielectric constant for homologous series of organic liquids decreases with increasing number of carbon atoms and with increasing molecular diameter.   J. F. S.

Molecular Association of Compounds of Carbon, Hydrogen, and Oxygen deduced from the Boiling Point and the Density at the Temperature. W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1022—1025).—The number of atoms in the molecule (n) of certain hydrocarbons and oxy-derivatives is given by the expression $n = (193M^2)/(T^2_{bp} \cdot d_{bp})$, in which M is the molecular weight, T_{bp} the absolute boiling point at one atmosphere, and d_{bp} the density at the boiling point.   A. J. W.

The Boiling Point Line of the System : Hexane–Nitrobenzene. E. H. Büchner (*Proc. K. Akad. Wetensch. Amsterdam,* 1917, **20**, 322—325).—When the boiling point of the mixture is plotted against the molecular proportion of nitrobenzene, a curve is obtained which indicates that the initial rate of increase in the temperature is large by comparison with the slow rate of increase for solutions containing 10—60% of nitrobenzene. The curve is inflected, and rises sharply as the proportion of nitrobenzene is further increased. This form of curve has been found previously for several pairs of liquids of limited miscibility at temperatures above the critical solution temperature.

The boiling point data indicate that this pair of liquids does not exhibit a maximum vapour pressure. This is in agreement with the general rule according to which such maxima are not to be expected when the boiling points of the components differ by more than about 100°. H. M. D.

The Diffusion of Mercury Vapour in a Vacuum. Marcel Guichard (*Bull. Soc. chim.,* 1917, [iv], **21**, 237—238).—To prevent the diffusion of mercury vapour from the pump to a tube, which contains a substance capable of absorbing mercury vapour and is being evacuated, it is advised either to introduce a second tube containing the same substance between the experimental tube and the pump, or to interpose a tube cooled sufficiently to cause the mercury vapour to condense. W. G.

Kinetic Theory of the Ideal Dilute Solution. S. A. Shorter (*Phil. Mag.,* 1917, [vi], **34**, 521—525).—A criticism of the arguments set forth by Tinker in a recent paper on the theory of binary liquid mixtures (A., 1917, ii, 294). This theory, which is based on the application of the Dieterici equation to binary mixtures, was said to lead to Raoult's law. The author points out that the deduction involves a mathematical error, and when this error is corrected, the theory yields a relation which is quite different from Raoult's law. A similar error is involved in the deduction of the expression for the osmotic pressure of a dilute solution, and the supposed agreement between observation and theory is fictitious. The failure of the theory when applied to actual facts is attributable to the circumstance that it takes no account of changes in the intermolecular forces which ensue when the solute is added to the solvent. H. M. D.

Kinetic Theory of the Ideal Dilute Solution. Frank Tinker (*Phil. Mag.,* 1917, [vi], **34**, 526—527).—A reply to Shorter's criticism of the author's theory (compare previous abstract). H. M. D.

The Structure of the Crystalline Forms of Silica, Iron Disulphide, Zinc Sulphide, and Calcium Carbonate. J. Beckenkamp (*Centr. Min.,* 1917, 353—365, 393—407. Compare A., 1917, ii, 296).—The axial ratios of quartz and of tridymite are

very closely related to those of rhombohedra derived from the cube, one diagonal of the cube being considered the trigonal axis of the rhombohedron. The author considers that the structures of these crystals as well as those of pyrites, zinc blende, sodium and potassium chlorides, calcspar, etc., are closely related to the face-centred cubic lattice. This conclusion is in agreement with the author's theory of the relationship between the atomic weights of the elements and the sizes of the spheres of influence of the atoms which determine the inter-atomic distances in the crystal. The author does not accept the structure for quartz suggested by Bragg.

E. H. R.

The Colloidal Nature of Colophony. I. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 115—121).—See this vol., i, 25.

Stability of Emulsions in the Constricted Tube and Marble Device for Anaerobiosis. IVAN C. HALL (*J. Physical Chem.*, 1917, **21**, 609—622).—The stability of oil–water emulsions in certain forms of culture tube has been found to be due to the protection from evaporation which these devices afford. Methods for the distinction of disperse phase from dispersive medium are discussed. [See also *J. Soc. Chem. Ind.*, 1917, **37**, 13A.]

H. M. D.

The Temperature of Ignition of Gaseous Mixtures. JAMES WALLACE McDAVID (T., 1917, **111**, 1003—1015).—In most of the methods previously employed for the determination of the ignition-temperature, the possibility is not excluded that slow combustion occurs before the ignition-temperature is reached, with the result that sufficient heat is generated to raise the remainder of the gaseous mixture to its ignition point. A new method is described in which the time factor is eliminated as far as possible, the method consisting in the ignition of a small volume of the gaseous mixture, contained in a soap bubble, by means of an electrically heated wire or other red hot body, the temperature being noted at which ignition just takes place.

The ignition temperatures of mixtures of various inflammable gases with air have been determined, and the results obtained show that the method not only gives a sharp ignition point, but that it is very suitable for comparative determinations. When the soap bubbles are not too large, instantaneous ignition occurs, and the ignition temperatures obtained under these conditions are regarded as the true values. When larger bubbles are used, the inflammable mixture ignites at a somewhat lower temperature, but this is probably due to the fact that slow combustion precedes the ignition, which is quite perceptibly delayed.   H. M. D.

The "Uniform Movement" during the Propagation of Flame. WALTER MASON and RICHARD VERNON WHEELER (T., 1917, **111**, 1044—1057).—According to the theoretical considerations advanced by Mallard and Le Chatelier (*Ann. des Mines*, 1883, [viii], **4**, 274), the speed of the "uniform movement," which

characterises the propagation of flame through inflammable mixtures under suitable conditions, should be directly proportional to $(T'-t)$ and inversely proportional to $(t-\theta)$, where T is the combustion temperature, t the ignition temperature, and θ the initial temperature of the combustible mixture, provided that the mixtures considered have the same thermal conductivity.

In order to obtain data to test this conclusion, measurements have been made of the velocity of the "uniform movement" in a series of mixtures of methane, oxygen, and nitrogen. The ignition temperatures have also been determined and the combustion temperatures calculated. It is found that the above relation is very nearly true so long as the oxygen in the mixtures is in excess of that required for complete combustion. When the amount of oxygen present is less than this, the observed velocity of the "uniform movement" is less than that calculated from the ratio $(T-t)/(t-\theta)$. In the case of upper limit mixtures, the deviation is considerable. From this it is inferred that the calculated combustion temperature is not attained when the oxygen is deficient in quantity, for in these circumstances the combustion process is more protracted, and there is consequently an increased radiation loss through the walls of the tube during the propagation of the flame.

With regard to the influence of the diameter of the tube on the speed of the "uniform movement," Mallard and Le Chatelier arrived at the conclusion that the speed will not be appreciably affected if the diameter is sufficiently great. This is probably true for tubes from 5 to 10 cm. in diameter, but in wider tubes the influence of convection currents introduces a factor which affects the speed to a considerable extent. Measurements of the speed for mixtures of methane and air in tubes varying from 2·5 to 96·5 cm. in diameter show that convection effects increase the speed in the wider tubes. It would thus seem that the "uniform movement" is a strictly limited phenomenon obtainable only in tubes of which the diameter is large enough to prevent appreciable cooling by the walls, but small enough to suppress the disturbing influence of convection.

The conditions necessary for obtaining the "uniform movement" of flame are discussed, and, in particular, attention is directed to the importance of the method of ignition.　　　　H. M. D.

Kinetics of the Alkaline Saponification of the Esters of Carbonic Acid. Anton Skrabal (*Monatsh.*, 1917, **38,** 305—318). —The rate of saponification of methyl and ethyl carbonate has been investigated at 25° in solutions containing sodium carbonate. The progress of the reaction, which may be represented by the equation $R_2CO_3 + Na_2CO_3 + 2H_2O = 2NaHCO_3 + 2ROH$, was followed by titration with $0·1N$-hydrochloric acid in presence of phenolphthalein. The results obtained show that the rate of saponification of the esters is proportional to the concentration of the ester and of the hydroxyl ion. For the methyl ester, the bimolecular velocity coefficient $k = 5·4$, and for the ethyl ester

$k = 1\cdot6$. These numbers are of the same order of magnitude as the coefficients for the corresponding esters of acetic acid. In acid solution, the esters are hydrolysed very slowly.

Experiments made with sodium ethyl carbonate show that the second stage of the alkaline saponification takes place with very great velocity, and that this is also characteristic of the hydrolysis in acid solution. The kinetic data are discussed in reference to the constitution of carbonic acid, and in explanation of the relative rates of the first and second stages of hydrolysis, it is suggested that the second stage is not really a hydrolytic process, but is to be regarded as an intramolecular change corresponding with the equation $OH\cdot CO\cdot OR = CO_2 + R\cdot OH$.   H. M. D.

The Velocity of the Alkaline Saponification of Formic Esters. ANTON SKRABAL and ADOLF SPERK (*Monatsh.*, 1917, **38**, 191—201).—The rate of saponification of methyl and ethyl formate has been measured at 0° and at 25° by using a mixture of potassium iodide and iodate as dynamic regulator. In view of the fact that the esters form additive compounds with potassium tri-iodide, the active mass of the ester during the later stages of the reaction is less than that which would be calculated from the thiosulphate titrations of the liberated iodine. For this reason, the calculated saponification velocity coefficient falls as the reaction proceeds, and the correct values can only be obtained from the initial stages. These initial measurements give $k = 2\cdot4 \times 10^3$ for methyl formate and $k = 1\cdot4 \times 10^3$ for ethyl formate at 25°. These values are in agreement with those previously obtained by indirect measurements according to an electrochemical method (Eucken, A., 1910, ii, 279).   H. M. D.

Consecutive Reactions. The Saponification of Methyl Oxalate in Solutions containing Iodide and Iodate. ANTON SKRABAL (*Monatsh.*, 1917, **38**, 159—189).—In the use of regulator mixtures for controlling the concentration of one of the reacting substances or one of the reaction products during the progress of a reaction, it is necessary to distinguish between static and dynamic regulators. In the case of static regulators, the velocity of the regulator reaction is very large in comparison with that of the reaction investigated, whilst the velocity of the regulator reaction may be of the same order or even much smaller than that of the reaction under examination if the regulator mixture is of the dynamic type. It is shown that the progress of a reaction which is regulated by a mixture of the dynamic group is such that the velocities of the two are mutually influenced in such a way that they keep in step. Whilst a mixture of the salts Na_2HPO_4 and NaH_2PO_4 acts as a static regulator in controlling the hydrogen ion concentration of a solution, a mixture of potassium iodide and iodate behaves as a dynamic regulator.

This mixture has been used in the determination of the velocity coefficients corresponding with the first and second stages in the

saponification of methyl oxalate. From the observed rate at which iodine is formed, it is possible to calculate the saponification coefficients. The experiments with methyl oxalate and potassium methyl oxalate give $k = 1.2 \times 10^6$ for the first stage and $k = 1.94 \times 10^2$ for the second stage respectively. These values agree satisfactorily with those obtained in previous measurements, in which use was made of a static regulator.

Comparison of the two series of experiments shows that the determination of the rate of saponification of methyl oxalate can be effected much more conveniently and accurately by using an iodide-iodate mixture as regulator than by the use of a mixture of sodium dihydrogen and disodium hydrogen phosphate. It is probable that the use of iodide-iodate mixtures may be found useful in the investigation of many other reactions which proceed with conveniently measurable velocity when the hydrogen ion concentration is not far removed from that corresponding with the neutral point. H. M. D.

History of Catalysis. H. J. PRINS (*Chem. Weekblad*, 1917, **14**, 1000—1004).—A polemical paper in support of the author's views on catalysis, and criticising Böeseken's "dislocation theory."
A. J. W.

Contact Catalysis. II. Fractional Combustion. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 644—675. Compare A., 1917, ii, 566).—The paper consists for the most part of extracts from the literature relating to the fractional combustion of gases, and attention is directed to the circumstance that these observations afford many examples of the selective influence of catalysts in determining the nature of the final products. At low temperatures, the influence of solid catalysts is very marked, and is one of the chief factors in determining which of two combustible gases will burn the more rapidly. At high temperatures, the influence of solid catalysts is greatly reduced and may be negligible, the reaction in this case taking place in the gaseous phase.

By suitably varying the solid catalyst, it should be possible to realise all the possible intermediate stages in the fractional combustion of a mixture of two combustible gases from the complete combustion of the one to the complete combustion of the other.
H. M. D.

Contact Catalysis. Decomposition of Ethyl Alcohol. CARL J. ENGELDER (*J. Physical Chem.*, 1917, **21**, 676—704).— When the vapour of ethyl alcohol is passed over heated metallic oxides or finely divided metals, it decomposes with the formation of ethylene and water or acetaldehyde and hydrogen, and the relative quantities of the two sets of products vary with the nature of the solid catalyst.

Experiments made with alumina, silica, zirconium dioxide, and titanium dioxide show that the ratio of ethylene to hydrogen in

the product of the reaction is reduced by mixing the alcohol with water. Similarly, it has been found that the addition of hydrogen to the alcohol vapour increases the proportion of ethylene when titanium dioxide is used as catalyst. Further observations with this catalyst at 400° show that acetaldehyde is not decomposed to any great extent into methane and carbon monoxide, but that it promotes the formation of ethane by combination of ethylene and hydrogen.

Ethyl ether when passed over alumina at 380° is decomposed almost quantitatively into ethylene and water. With titanium dioxide, the dehydrating action takes place very slowly. At 210°, ethyl alcohol, when passed over alumina, gives ethyl ether as the chief product. H. M. D.

The Determination of Atomic Weights. MARCEL GUICHARD (*Bull. Soc. chim.*, 1917, [iv], **21**, 238—241).—A general criticism of the methods used for determining atomic weights. Three conditions for such methods are given, namely: (1) as far as possible, analyse or synthesise oxygenated compounds; (2) perform simple chemical reactions only requiring a very small number of auxiliary substances, avoiding contact with water, air, or inert gases; (3) use complete methods, where all the compounds utilised or formed are weighed. W. G.

Variable Atomic Weights, with some Reference to Geologic Time. H. S. SHELTON (*Chem. News*, 1917, **116**, 259—261).—A criticism of the theory of isotopes in which the author contends that the known facts do not warrant the conclusion that isotopic elements are inseparable.

Estimates of geologic time based on radioactivity data are probably not nearly so precise as the statements of certain workers on radioactive problems would suggest. In view of the possible errors which are inherent in such estimates, it is considered that the radioactivity estimates are only of value in indicating the order of geologic eras. H. M. D.

Atomic Frequency and Atomic Number. Frequency Formulæ with Empirical Constants. H. STANLEY ALLEN (*Phil. Mag.*, 1917, [vi], **34**, 478—487).—It is probable that some connexion exists between the characteristic frequency v of an element in the solid state and its atomic number N, and an attempt is made to establish this by making use of the various formulæ which have been put forward to express the relation between the atomic frequency and other physical properties. These formulæ are more or less empirical, and in some cases yield values for the atomic frequency which differ appreciably. For the majority of the elements, however, the calculated frequencies are found to satisfy the relation $Nv = nv_A$, in which n is a whole number (the frequency number) and v_A a constant. The same element may have different frequency numbers for the different forms of the

solid element, but, broadly speaking, the value of n varies in a periodic manner with the atomic number. The mean value of v_A for the metallic elements is $21\cdot3 \times 10^{12}$.   H. M. D.

Electronic Frequency and Atomic Number. H. Stanley Allen (*Phil. Mag.*, 1917, [vi], **34**, 488—496. Compare preceding abstract).—The electron frequencies calculated from the maximum of the selective photo-electric effect, from the limiting photo-electric frequency, from the ionisation potential of gases, and from thermionic potentials appear to be related in a simple manner with the atomic number N of the element concerned. If v is the calculated electron frequency, then $Nv = nv_e$ or $Nv = (n + \frac{1}{2})v_E$, in which n is an integer and v_E is the fundamental electronic frequency $= 3\cdot289 \times 10^{15}$. The fundamental electronic frequency is thus about 154 times the fundamental atomic frequency v_A.   H. M. D.

Formulation of the Law of Multiple Proportions. D. Balareff (*J. pr. Chem.*, 1911, [ii], **95**, 397—398).—It is pointed out that it is only in the case of simple series of compounds of two elements that the masses of the one element which unite with the same mass of the other element are to one another in the ratio of simple integers. For example, whilst the masses of carbon which unite with one part of hydrogen are in methane, ethylene, and acetylene respectively 3, 6, and 12, in methane, ethane, propane, hexane, eicosane, and anthracene they are 3, 4, 4·5, 5·143, 5·714, and 16·8. It would be better, therefore, to express the law as "The masses of the different elements in a compound are directly proportional to their equivalent weights or to simple multiples of their equivalents."   J. C. W.

Absolute Determinations of Mass by means of the Micro-balance. J. Kramer (*Chem. Zeit.*, 1917, **41**, 773—774).— The ordinary form of torsion micro-balance is not suitable for direct weighings, and experiments have accordingly been made to ascertain the applicability of a balance of the usual type in the determination of the weights of small quantities of substance. The balance described has a carrying capacity of 1 gram, the length of the beam is 154·4 mm., and its weight 7·825 grams. The addition of 0·1 mg. produces a displacement of the pointer amounting to 48 divisions when the balance is unloaded, and this decreases to 35 divisions for a load of 100 mg. and to 10 divisions for a load of 1000 mg. Each division on the scale represents 0·35 mm.

The results obtained with the balance, when suitable precautions are taken, are said to be quite satisfactory.   H. M. D.

Exact Weighings. Marcel Guichard (*Bull. Soc. chim.*, 1917, [iv], **21**, 233—235).—An examination of the temperature differences between the two arms of a balance, due to the variation of external conditions.   W. G.

The Limitations of the Balance. Bertram Blount (T., 1917, **111**, 1035—1039).—Series of weighings made by three independent observers on six balances of the best make showed variations

ranging from 0·4 to 1·6 mg. during a period of four months. These variations cannot be correlated with any known variation in the external conditions. The author is inclined to attribute the observed inconstancy to variations in the effective length of the arms of the balance resulting from fortuitous movements of the knife-edges. H. M. D.

The Weighing of Evacuated Tubes. MARCEL GUICHARD (*Bull. Soc. chim.*, 1917, [iv], **21**, 235—237).—The author prefers to use a sealed tube rather than one closed by a tap, and describes a method of weighing such an evacuated tube, filling it with gas, and determining the weight of gas thus entering. W. G.

The Centenary of Charles Gerhardt. (*Suppl. Bull. Soc. chim.*, 1916, 1—108).—An account of the proceedings of the meeting of the Société chimique de France on December 8th, 1916, in celebration of the centenary of Charles Gerhardt. There is included in it a full account of Gerhardt's life and work by M. Marc Tiffenau, and a chronological list of his publications.

Inorganic Chemistry.

Action of Hydrogen Peroxide Solution on Lime-water and Iodine: Preparation of Ammonium Iodide. T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1917, **54**, 1373—1374).—In presence of hydrogen peroxide solution, iodine reacts with lime-water to form the iodide, with evolution of gas, and formation of only a trace of iodate. With ammonium hydroxide the reaction takes place in accordance with the equation $2NH_3 + I_2 + H_2O_2 = 2NH_4I + O_2$.   A. J. W.

Reaction between Ozone and Hydrogen Peroxide. VICTOR ROTHMUND and ALEXANDER BURGSTALLER (*Monatsh.*, 1917, **38**, 295—303. Compare A., 1913, ii, 773).—The velocity of the reaction between ozone and hydrogen peroxide has been examined in $0.01N$-sulphuric acid solution at $0°$, the two substances being separately estimated in the reaction mixture by the method described in a previous paper (A., 1913, ii, 524). In presence of relatively large quantities of hydrogen peroxide, the reaction may be represented by the equation $H_2O_2 + O_3 = H_2O + 2O_2$, and the rate of disappearance of the ozone follows closely the equation for a unimolecular reaction. When the ratio of hydrogen peroxide to ozone is smaller, the ozone disappears more rapidly than the hydrogen peroxide, and this inequality in the quantities of ozone and hydrogen peroxide which are destroyed in a given interval of time increases as the concentration of the hydrogen peroxide is reduced.

The facts suggest that the interaction between ozone and hydrogen peroxide is accompanied by the spontaneous decomposition of ozone and that hydrogen peroxide acts as a powerful catalyst in respect to the latter reaction. This theory also offers an explanation of previously recorded observations on the rate of decomposition of ozone in dilute sulphuric acid solution (compare A., 1913, ii, 489), for it is highly probable that the ozonisation of oxygen is accompanied by the formation of traces of hydrogen peroxide.

H. M. D.

The Valencies of Nitrogen. FRANZ WENGEL (*Monatsh.*, 1917, **38**, 267—293).—The author considers that no conclusive evidence has yet been put forward in support of the view that four of the nitrogen valencies bear the same relation to the fifth. Whilst certain chemical observations suggest that there are two pairs of valencies which are identical in relation to the fifth valency, physico-chemical data seem to indicate that there are three valencies which are identical with regard to the fifth valency. From this it is inferred that the fifth valency does not always represent one and the same valency unit.

An attempt is made to account for the behaviour of nitrogen compounds on the assumption that the valencies of nitrogen are divisible into two distinct groups, one of which includes two and the other three valencies which are equal in all respects. When quinquevalent nitrogen is transformed into tervalent nitrogen there is a loss of one valency from each group. This change is supposed to result in the formation of an intra-atomic double linking connecting dissimilar nuclei. In support of this theory attention is directed to the similarity between the amines and ethylene derivatives in respect of their capacity to form additive compounds.

It is said that this hypothesis affords a satisfactory account of the chemistry of nitrogen compounds. H. M. D.

Disodium Nitrite, an Additive Compound of Sodium Nitrite and Sodium. EDWARD BRADFORD MAXTED (T., 1917, **111**, 1016—1019).—When solutions of metallic sodium and sodium nitrite in anhydrous ammonia are mixed together, a brilliant, yellow substance is precipitated which has the composition Na_2NO_2. The same substance is deposited on the cathode when a solution of sodium nitrite in perfectly anhydrous liquid ammonia is subjected to electrolysis. The substance is decomposed vigorously by water with the formation of sodium nitrite, sodium hydroxide, and hydrogen. By passing a current of moist nitrogen over the disodium nitrite, the action is moderated, and the resulting solution is found to be free from hydroxylamine and hyponitrite.

H. M. D.

Formation of Large Crystals in Zinc Rods and Wire. W. FRAENKEL (*Zeitsch. Elektrochem.*, 1917, **23**, 302—304).—It has been observed that large crystals are often found in zinc rods which have been worked mechanically. The author describes experiments

made with the object of ascertaining the conditions under which these large crystals are formed and the reasons for their formation. Rods of zinc of varying diameter were subjected to a temperature just below the melting point of zinc for some time, and after cooling were broken and the structure of the break examined. In some cases it was found that a recrystallisation of the metal had occurred, and that the cross-section of the break consisted of a single crystal, whilst in other cases only small crystals were observed. The author suggests possible explanations of the phenomenon, but is unable to decide on any one of the suggestions as the cause. A number of microphotographs of sections of zinc rods before and after treatment are given in the paper.   J. F. S.

Action of Hydrogen Peroxide on the Neutral Salts of Lead.

V. ZOTIER (*Bull. Soc. chim.*, 1917, [iv], **21**, 241—243. Compare A., 1913, ii, 216, 465).—Neutral lead salts exert a more or less marked catalytic action on hydrogen peroxide. Using hydrogen peroxide (100 vols.), the catalysis is intense with soluble organic salts, and feeble with insoluble organic salts or mineral salts. With lead acetate one portion of the hydrogen peroxide yields lead peroxide, which then reacts with the remainder of the hydrogen peroxide, and at the end of the reaction there is no lead peroxide left. If the solid salt is used, the catalysis is at first moderate, but soon becomes violent and the mass becomes hot. The presence of acids lessens or hinders the catalysis by hindering the preliminary formation of the lead peroxide. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 7A.]
          W. G.

Some Compounds of Lead.

V. ZOTIER (*Bull. Soc. chim.*, 1917, [iv], **21**, 244—246. Compare A., 1913, ii, 216, 465, and preceding abstract).—Pure lead peroxide may be prepared by the addition of hydrogen peroxide to a solution of lead nitrate in 20% sodium hydroxide. Hydrogen peroxide may be used to differentiate between a normal and a basic lead salt. With the former it does not give any residual lead peroxide, but with the latter it does. Alkaline solutions of lead salts may be used as a delicate test for hydrogen peroxide, or conversely hydrogen peroxide in the presence of sodium hydroxide may be used as a delicate test for lead.

Contrary to the general opinion, it is found that lead peroxide is slowly attacked by mineral acids or aqueous solutions of alkali hydroxides. The process is, in all cases, very slow, the rate varying with the acid or alkali used.

By heating together at 150° equal weights of lead nitrate and 50% sodium hydroxide, an amorphous red lead is obtained, but if the proportion of lead salt is halved and the temperature raised to 160°, a microcrystalline red oxide is obtained. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 7A.]   W. G.

The Dissociation Constants of Mercury Hydroxides.

I. M. KOLTHOFF (*Chem. Weekblad*, 1917, **14**, 1016—1022).—The

dissociation of mercury hydroxide solution is a step-by-step process, and can be represented by the scheme

$$Hg(OH)_2 \rightleftarrows HgOH^{\cdot} + OH'; \quad HgOH^{\cdot} \rightleftarrows Hg^{\cdot\cdot} + OH'.$$
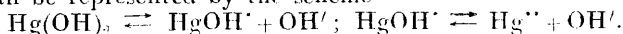
A. J. W.

Quantitative Investigations on the Corrosion of Resistant Glass by Sodium Hydroxide. C. J. VAN NIEUWENBURG (*Chem. Weekblad*, 1917, **14**, 1034—1040).—A comparison of the effects produced by heating sodium hydroxide solution in Jena and Laborax flasks.   A. J. W.

The Production of Colloidal Base Metals by Reduction of Solutions or Suspensions of Compounds at Higher Temperatures in the Presence of Protective Substances. Colloidal Nickel. C. KELBER (*Ber.*, 1917, **80**, 1509—1512).—The knowledge that near 200° nickel oxide and some nickel salts can be reduced to metallic nickel by hydrogen, has been applied to the production of colloidal nickel by reducing solutions or suspensions in glycerol containing gelatin or gum arabic as a protective colloid. For example, a solution of nickel formate and gelatin in glycerol at 200—210° when submitted to the action of a stream of hydrogen assumes a chestnut-brown colour. The colloidal solution remains unaltered in the air and is miscible with alcohol, but on treatment with water and centrifuging deposits the colloidal metal as a dark brown solid, containing 25—30% of nickel, which can again yield colloidal nickel solutions in dilute acetic acid, acidified water, glycerol, or alcohol.

Other reducing agents can be applied to the same purpose; nickel formate at 220° in glycerol solution in the presence of gelatin, is reduced by hydrazine hydrate with formation of a colloidal nickel solution of similar properties to that just described. Formaldehyde, hydroxylamine, and hypophosphorous acid can also be applied as reducing agents for the purpose, whilst gum arabic can be used in place of gelatin. The nickel formate can be replaced by nickel acetate or freshly precipitated nickel hydroxide.   D. F. T.

Iso- and Hetero-poly-acids. XV. Critical Researches on the Constitution of the Hetero-poly-acids. ARTHUR ROSENHEIM and JOHANNES JÄNICKE (*Zeitsch. anorg. Chem.*, 1917, **100**, 304—354. Compare A., 1913, i, 413; ii, 59; 1914, ii, 58; 1915, ii, 266, 468; 1916, ii, 333, 334; 1917, ii, 35).—A historical and theoretical paper in which the crystallographic, physical, and chemical properties of the iso- and hetero-poly-acids are summarised and the whole of the previous work is discussed. The earlier theories on the constitution of these acids are reviewed, including the application of Werner's co-ordination theory. The last is found to be unsatisfactory, but the modification of this theory suggested by Miolati (A., 1908, ii, 595) and extended by Rosenheim provides the most satisfactory elucidation of the constitution of these substances.   E. H. R.

Analytical Chemistry.

New Form of Safety Pipette. A. S. BEHRMAN (*J. Ind. Eng. Chem.*, 1917, **9**, 1047).—A three-way tap is attached to the top of an ordinary pipette by means of a short length of rubber tubing and a rubber bulb fitted with suitable valves is connected with the upper limb of the tap. The pipette is filled by pressing and releasing the bulb. The tap is then turned so as to admit air to the pipette, by which means the level of the liquid is lowered to the mark, and then delivered.   W. P. S.

Preparation of Ammonium Citrate Solution and the Estimation of Insoluble Phosphoric Acid. PHILIP McG. SHUEY (*J. Ind. Eng. Chem.*, 1917, **9**, 1045).—Neutral ammonium citrate solution may be prepared by dissolving 1814·37 grams of citric acid in 6961 c.c. of water and 1760 c.c. of 28% ammonia, the water and ammonia being measured at 23°. The insoluble phosphoric acid in acid phosphate may be estimated with practically identical results, whether or not the weighed portion has been washed previously with water, and preliminary washing of samples containing cyanamide does not appear to be necessary. It may be important to use a neutral ammonium citrate solution in the case of ground tankage, whale guano, meat guano, fish, and similar materials which have not been strongly acidified.   W. P. S.

Micro-method for the Estimation of Inorganic Phosphates in the Blood-serum. W. McKIM MARRIOTT and F. H. HAESSLER (*J. Biol. Chem.*, 1917, **32**, 241—243).—Full details of the method previously described (compare Howland, Haessler, and Marriott, A., 1916, ii, 269).   H. W. B.

The Perchlorate Method for the Estimation of the Alkali Metals. F. A. GOOCH and G. R. BLAKE (*Amer. J. Sci.*, 1917, [iv], **44**, 381—386. Compare A., 1917, ii, 270).—In this method it is unnecessary to use an alcoholic liquid saturated with the substance to be precipitated, since the volume of the solution (97% alcohol containing 0·1% of perchloric acid) used for washing the precipitate may be so restricted that the solubility of the precipitated perchlorates is insignificant. A single evaporation with a moderate excess of perchloric acid (0·1 c.c. for each 0·1 gram of salt) is not sufficient to convert considerable quantities of alkali chlorides (for example, 0·3 gram) completely into perchlorate; the residue should be treated with a further quantity of perchloric acid and again evaporated. For the separation of large amounts of insoluble perchlorates from sodium perchlorate, the washed precipitate should be dissolved in a small volume of water and the evaporation with perchloric acid repeated. In the case of rubidium perchlorate, the precipitate should be digested for fifteen minutes with the alcoholic washing solution. It is to be noted that perchloric acid has a distinct solvent action on glass. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 21A.]   W. P. S.

Micro-method for the Estimation of Calcium and Magnesium in Blood-serum. W. McKim Marriott and John Howland (*J. Biol. Chem.*, 1917, **32**, 233—239).—Full details of the method previously described (compare Howland, Haessler, and Marriott, A., 1916, ii, 269). H. W. B.

Estimation of the Metal Content of Powdered Metals. F. Hodes (*Zeitsch. angew. Chem.*, 1917, **30**, 240).—The quantity of metallic tungsten in powdered tungsten which has been prepared by reduction with carbon may be estimated by igniting a portion of the sample in an open crucible; the increase in weight is due to oxidation of the metal to tungsten trioxide. As, however, the powdered metal usually contains small quantities of carbon and moisture, it is necessary to heat another portion of the sample in a current of oxygen, weigh the amounts of carbon dioxide and water given off, and correct the first weight accordingly. W. P. S.

Iodometric Estimation of Copper and Iron. Herm. Ley (*Chem. Zeit.*, 1917, **41**, 763).—Soluble cupric and ferric salts both liberate iodine from potassium iodide in acetic acid solution, and the iodine set free is a measure of the amount of cupric and ferric salts present. When it is desired to estimate copper in the presence of iron, the latter may be precipitated as ferric phosphate, which is insoluble in acetic acid and does not react with potassium iodide; cupric phosphate, however, is readily soluble in acetic acid. The solution containing the cupric and ferric salts is treated with sodium phosphate solution, then acidified with acetic acid, potassium iodide is added, and the iodine is titrated with thiosulphate solution. The ferric salt is estimated by treating another portion of the original solution with potassium iodide and acetic acid, and titrating the liberated iodine; the difference between the volumes of thiosulphate solution used in the two titrations is equivalent to the quantity of ferric salt present. Aluminium and zinc do not interfere. W. P. S.

Sensitive Reaction of Hydrogen Peroxide depending on the Formation of Dihydroxytartaric Acid. G. Denigès (*Ann. Chim. anal.*, 1917, **22**, 193).—A violet coloration is formed when a small quantity of dilute hydrogen peroxide solution is added to a mixture of 2 c.c. of 5% tartaric acid solution and 2 drops of 5% ammonium ferrous sulphate solution, and the mixture then treated with 6 drops of sodium hydroxide solution. The reaction may be obtained with a quantity of hydrogen peroxide not exceeding 0·05 mg. W. P. S.

Estimation of Glycerol by the Iodide Method, using Small Quantities of Hydriodic Acid (Semimicro-iodide Method). R. Neumann (*Zeitsch. angew. Chem.*, 1917, **30,** 234—237).—The author finds that this method (compare A., 1902, ii, 111, 585; 1903, ii, 515) yields trustworthy results when only

about one-tenth of the usual quantities of sample and reagents are employed. The apparatus used has about one-eighth of the capacity of the iodide apparatus described by Stritar (A., 1904, ii, 95).

W. P. S.

Oxidation of Organic Compounds with Chromic Acid.

A. WINDAUS (*Zeitsch. physiol. Chem.*, 1917, **100**, 167—169).—Certain organic compounds readily yield acetone and acetaldehyde when treated with chromic acid. The products can be separated by distillation and recognised by conversion into the comparatively insoluble *p*-nitrophenylhydrazones. In this way, cholesterol, coprosterol, and sitosterol, containing an *iso*propyl group, can be readily distinguished from the somewhat similar bile acids, which do not yield any acetone or aldehyde when oxidised by chromic acid.

Methylpentoses, such as rhamnose, are similarly easily detected in the presence of other pentoses and hexoses by means of the chromic acid oxidation test. The test must be carried out under the prescribed conditions, involving the use of a solution of chromic acid in glacial acetic acid. If an excess of sulphuric acid is substituted for the glacial acetic acid, lævulose, and even dextrose, are found to yield acetaldehyde and other volatile products, which can form iodoform and insoluble *p*-nitrophenylhydrazones (compare Engfeldt, A., 1917, ii, 550).

H. W. B.

Formaldehyde as a Negative Catalyst in Sugar Reactions.

H. MAGGI and G. WOKER (*Ber.*, 1917, **50**, 1331—1335).—Formaldehyde hinders the reducing action of dextrose or maltose in the Moore-Heller and Rubner tests, and especially the reduction of methylene-blue or picramic acid. Although formaldehyde has a more powerful reducing action on Nylander's solution than the sugars, mixtures of them containing 1 c.c. of 40% formaldehyde to 0·5 c.c. of 1% dextrose or maltose do not affect this reagent. The aldehyde also hinders the reduction of Fehling and Pavy solutions by dextrose or maltose.

J. C. W.

Malic Acid and Citric Acid.

T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1917, **54**, 1371—1373).—Both malic acid and citric acid answer to the iodoform test, but can be distinguished by the fact that barium malate is not precipitated either in neutral solution or in presence of acetic acid.

A. J. W.

Probable Accuracy, in Whole Blood and Plasma, of Colorimetric Estimations of Creatinine and Creatine.

ANDREW HUNTER and WALTER R. CAMPBELL (*J. Biol. Chem.*, 1917, **32**, 195—231. Compare Wilson and Plass, A., 1917, i, 360, and Gettler and Oppenheimer, A., 1917, ii, 184).—The authors have prepared a series of curves showing the rate at which the colour utilised as the basis of a creatinine estimation develops, not only in pure aqueous solutions, but also in the various circumstances

in which it is applied to the analysis of blood. A comparison of these curves reveals the presence or absence of substances capable of producing a colour similar to that arising from creatinine. In plasma, the only substance capable of simulating the reaction for creatinine is dextrose, and its influence on the estimation of creatinine is shown to be too small to have much practical importance. In whole blood, however, an unknown substance is present which, although reacting more slowly than creatinine, contributes in the Folin technique an appreciable fraction of the total colour developing within ten minutes. On laking the blood, a much larger amount of this unknown substance is set free and passes into the protein-free filtrate. The filtrates from autoclaved blood or plasma also contain relatively large quantities of the substance which reacts similarly to creatinine.

A consideration of these results indicates that although the Folin method estimates the preformed creatinine of plasma with a satisfactory approximation to accuracy, the results obtained by the same method for the preformed creatinine of whole blood are on the average about 50% higher than the truth. The technique of Myers leads to a still greater exaggeration of the preformed creatinine of blood. The Folin method for creatine, whether applied to whole blood or to plasma, also gives decidedly erroneous results, liable to be in the former case about twice and in the latter about four times as high as the amount actually present.

H. W. B.

Estimation of Fæcal Indole. OLAF BERGEIM (*J. Biol. Chem.*, 1917, **32**, 17—22).—The fæces are mixed with potassium hydroxide solution and the indole distilled over in an ordinary Kjeldahl distillation apparatus. Any ammonia in the distillate is removed by a second distillation after acidifying with dilute sulphuric acid. The final distillate is treated with sodium β-naphthaquinonesulphonate and alkali, and the blue indole compound formed extracted with chloroform and estimated colorimetrically (compare Herter and Foster, A., 1906, ii, 134, 910).   H. W. B.

Improvement of the Volumetric Method of Estimating Albumin by means of Potassium Ferrocyanide. Presence of Rapidly Decomposable Proteins in certain Urines. ED. JUSTIN MUELLER (*Bull. Sci. Pharmacol.*, 1917, **24**, 221—224; from *Chem. Zentr.*, 1917, ii, 325. Compare A., 1917, ii, 555).—In the previous communication the author has described a method of estimating albumin in urine, and pointed out that the immediate occurrence of the colour change with iron alum (after addition of 3·5 c.c. of potassium ferrocyanide necessary for the saturation of the acidified water) is indicative of the absence of albumin. Subsequently, however, it has been observed that the colour change can also occur in the presence of readily decomposable proteins. These differ from the albumins known in urology. They do not yield a precipitate when warmed or when treated with acetic acid.

They are precipitated by warm trichloroacetic acid and give precipitates with cold trichloroacetic acid, cold nitric acid, and Esbach's reagent, which gradually dissolve when warmed. A cold solution of potassium ferrocyanide in acetic acid yields a precipitate which is stable when warmed; saturated ammonium sulphate or sodium acetate solution gives a precipitate soluble in water, whilst precipitates are not produced by sodium chloride or magnesium sulphate. The proteins are readily hydrolysed when warmed or in acetic acid solution. They are rendered more stable by addition of ammonium sulphate.

For the volumetric estimation, urine (50 c.c.) is treated with so much finely divided ammonium sulphate (8—9 grams) that a volume of 55 c.c. is attained; the solution is filtered, and 11 c.c. of the filtrate are used for the titration.   H. W.

Adaptation of Winkler's Method to Biological Work. W. J. V. OSTERHOUT and A. R. C. HAAS (*J. Biol. Chem.*, 1917, **32**, 141—146).—The apparatus consists of two glass tubes 30 cm. long and 27 mm. in diameter joined together by rubber tubing and furnished with rubber stoppers at the free ends (all the rubber tubing and stoppers used in the apparatus should be coated with paraffin). One of the rubber stoppers is connected with a series of smaller glass tubes (13 mm. inside diameter) joined by rubber tubing with only enough space between them to permit the insertion of a clamp. The larger tubes are filled with the solution containing the organisms of which the oxygen metabolism is to be investigated. To estimate the oxygen in the solution at any time, the organisms are first allowed to gravitate to the bottom of the two tubes, and then the lower one, containing the organisms, is clamped off and removed. The smaller tubes are then filled successively with alkaline potassium iodide, manganese chloride, and concentrated hydrochloric acid, each being separated from the other by means of the clamps. By releasing the clamps, the reagents are successively introduced into the oxygenated solution, and finally the contents are run into a beaker and titrated with thiosulphate, as in Winkler's method for the estimation of oxygen in solutions.

The advantages claimed for the apparatus are that it permits the removal of the organisms before adding the reagents, and also the addition of the reagents without danger of contamination by oxygen. Modifications are described whereby it is possible to take samples of the solution for analysis at intervals during an experiment.   H. W. B.

General and Physical Chemistry.

The Arc Spectrum of Tantalum on the International Scale. HEDWIG JOSEWSKI (*Zeitsch. wiss. Photochem.*, 1917, **17**, 79—96).—Accurate measurements have been made of the wavelengths of lines in the arc spectrum of tantalum between λ 7000 and λ 2430. The observations, which are compared with those obtained previously by Exner and Haschek, also afford information relative to the intensity and the sharpness of the lines.

There is no evidence of the occurrence of pairs of lines with a constant difference of frequency as suggested by Paulson (compare A., 1915, ii, 196). H. M. D.

The Photographic Spectra of Meteorites. SIR WILLIAM CROOKES (*Phil. Trans.*, 1917, [*A*], **217**, 411—430).—The spectra of thirty meteorites have been examined with the aid of a spectrograph characterised by certain novel features, which are described. The use of a quartz slit has given very satisfactory results, the difficulty attending the production of a true knife-edge being solved by making a very narrow bevel on the front of the quartz plate and thereby producing a jaw with an angle of 90°. The bevelled edge is quite opaque in consequence of refraction, and to prevent light passing through the flat part of the plate, the plane surface of the quartz was coated with gold by cathode deposition.

The most striking result derived from the spectral examination of the thirty aerolites is the similarity in composition and the small number of elements which are present. Making due allowance for differences in the photographic activity of the elements in their arc spectra, it is found that only ten of the known elements are present. These elements are iron, chromium, magnesium, nickel, silicon, sodium, manganese, potassium, aluminium, and calcium, and of these, the first four only are present in quantity. Excepting the results for three aerolites, it is found that the relative proportions of the several elements are approximately the same in all. This suggests that the aerolites have a common origin in the disruption of some stellar body for which the process of cosmical evolution is complete. The siderites would appear to have a different origin, or may possibly have formed the solid nucleus or core from which the chromium and other elements have been separated, leaving the magnetic elements iron and nickel as a residue in the familiar ferronickel meteorites. H. M. D.

Hydrogen and Calomel Electrodes. GILBERT N. LEWIS, THOMAS B. BRIGHTON, and REUBEN L. SEBASTIAN (*J. Amer. Chem. Soc.*, 1917, **39**, 2245—2261. Compare Lewis and Randall, A., 1914, ii, 802).—The results of a number of investigations on (i) the potential of the hydrogen electrode in solutions of hydrochloric acid and

potassium hydroxide of various concentrations, (ii) the dissociation constant of water, (iii) the potential of calomel and silver chloride electrodes in solutions of potassium chloride and hydrochloric acid, (iv) methods of establishing definite and reproducible potentials at the boundaries between solutions, and (v) on improvements in the experimental technique of such determinations, are recorded at some length.   An electrolytic hydrogen generator which supplies a continuous stream of pure dry hydrogen is described.   Electrodes of gold coated with a layer of iridium are recommended as the most suitable for measuring hydrogen ion potentials, since they very rapidly acquire the correct potential and then remain constant. Pieces of apparatus are described in which the hydrogen, calomel, and silver chloride electrodes are most conveniently and accurately built up.   A device for maintaining a constant and easily reproducible surface of contact between two liquids is also described. All measurements were made at 25°, and the following results, each the mean of many experiments, are given in the paper:

1. $Hg, HgCl, KCl$ $0.1M \| N.E.$; $e = -0.0529$ volt.
2. $Hg, HgCl, HCl$ $0.1M \| KCl$ $0.1M, HgCl, Hg$; $e = 0.0278$ volt.
3. $Ag, AgCl, HCl$ $0.1M \| KCl$ $0.1M, AgCl, Ag$; $e = 0.0278$ volt.
4. $Ag, AgCl, HCl$ $0.01M \| KCl$ $0.01M, AgCl, Ag$; $e = 0.0272$ volt.

The values of the $E.M.F.$ in 2, 3, and 4 afford very good confirmation of the validity of the formula of Lewis and Sargent (A., 1909, ii, 369) for calculating the potential difference between liquid surfaces.

5. H_2, HCl $0.1M, HgCl, Hg$; $e = 0.3989$ volt.
6. H_2, HCl $0.1M \| KCl$ $0.1M, HgCl, Hg$; $e = 0.4267$ volt.

The value 0.4267 found for the combination 6 can be obtained by calculation from the experimental values of combinations 5 and 2.

7. H_2, HCl $0.01M, HgCl, Hg$; $e = 0.5105$ volt.   If this value is combined with that obtained from combination 8, the value of the combination 9 can be calculated.

8. $Hg, HgCl, HCl$ $0.01M \| KCl$ $0.01M, HgCl, Hg$; $e = 0.0272$ volt.
9. H_2, HCl $0.01M \| KCl$ $0.01M, HgCl, Hg$; $e = 0.5377$ volt.

The difference between the $E.M.F.$ of cells 5 and 7, that is 0.1116 volt multiplied by F' (23074), gives the free energy of dilution of hydrochloric acid, which equals 2573 cals.   From this value, the degree of ionisation of $0.1M$, $0.03M$, and $0.01M$ potassium chloride is found to be respectively $\alpha = 0.780$, 0.865, and 0.930.

Making use of the foregoing potential values, the value of the $E.M.F.$ of the normal calomel electrode is calculated in terms of the value of the normal hydrogen electrode.   The following values are obtained:

(a) $Hg, HgCl, HCl$ $0.1M \| KCl$ $0.1M, HgCl, Hg$; $e = 0.0012$ volt.
(b) $H_2, H^{\cdot}(M) \| HCl$, $0.01M$, H_2; $e = -0.0644$ volt.
(c) $H_2, H^{\cdot}(M) \| N.E.$; $e = 0.2828$ volt.

In all cases (*a*), (*b*), and (*c*), the contact potential is eliminated. Consequently, if the potential of the normal hydrogen electrode is taken as zero, the potential of the normal calomel electrode is -0.2828 volt.

10. H_2,KOH $0.1M \| KCl$ $0.1M$, $HgCl$,Hg; $e = 1.0833$ volts.
11. H_2,KOH $0.01M \| KCl$ $0.01M$, $HgCl$,Hg; $e = 1.0820$ volts.

The dissociation constant of water is calculated from the hypothetical combination $H_2,OH'(M) \| H^{\cdot}(M)H_2$; $e = 0.8278$ volt, and the value $K_w = 1.012 \times 10^{-14}$ obtained. It is shown that the values of the E.M.F. obtained when the gas pressure is changed do not vary more than 0.00001 volt from the values calculated from the thermodynamic equation. J. F. S.

Free Energy of Hydrochloric Acid in Aqueous Solution. II. ARTHUR A. NOYES and JAMES H. ELLIS (*J. Amer. Chem. Soc.*, 1917, **39**, 2532—2544. Compare A., 1916, ii, 369).—In continuation of previous measurements of the E.M.F. of cells of the type $H_2 | HCl | HgCl | Hg$, the authors have replaced the calomel electrode by a silver chloride electrode with the object of obtaining more accurate data for acid solutions of low concentration. Data are recorded for solutions varying in concentration from 0.3 to $0.001N$ at $15°$, $25°$, and $35°$. The changes in the free energy and total energy attending the transfer of one gram-molecule of hydrogen chloride from solutions of varying concentration to a $0.1N$-solution are calculated from the data, and it is inferred that hydrochloric acid is by no means completely ionised in $0.003N$-solution. On the assumption that the ionic activity and the ionic concentration can be regarded as equal in the case of this dilute solution, the authors have recalculated the activity coefficients for hydrochloric acid in solutions varying in concentration from 0.003 to $4.5N$. As before (*loc. cit.*), these activity coefficients are found to diverge from the conductivity ratio Λ/Λ_∞ by about 10% in the case of a $0.1N$-solution. The calculated activity coefficients diminish with increase in the concentration of the acid up to $0.5N$, but increase rapidly as the concentration of the acid is further increased. H. M. D.

Potential of the Bromine Electrode : Free Energy of Dilution of Hydrogen Bromide : Distribution of Bromine between Several Phases. GILBERT N. LEWIS and HYMAN STORCH (*J. Amer. Chem. Soc.*, 1917, **39**, 2544—2554).—A platinum iridium electrode immersed in a solution of potassium bromide or hydrobromic acid containing free bromine has been used in the determination of the potential of the bromine electrode by measurements of the E.M.F. of the cells obtained by combination of this with the calomel or the hydrogen electrode. The acid cell affords the more trustworthy results, and the value of the bromine potential for a solution containing bromine and bromide ion in molar concentration against the normal hydrogen electrode is found to be -1.0872 volts.

By measuring the *E.M.F.* of the cell $H_2|HBr|AgBr|Ag$ for HBr concentrations equal to $0·01$, $0·03$, and $0·1N$, it has been found that the ionic activity coefficients are very nearly equal to those previously found for HCl at the same concentrations.

The determination of the ratio of distribution of bromine between carbon tetrachloride and aqueous solutions of $0·001N$- and $0·1N$-hydrobromic acid has shown that the constant

$$K = [HBr_3]/[HBr][Br_2]$$

has nearly the same value as the constant for a solution in which the hydrobromic acid is replaced by potassium bromide.

By passing a current of dry air through solutions of bromine in carbon tetrachloride, it has been found that the vapour pressure of the bromine is proportional to the concentration of the solution when this is measured in terms of molar fractions.   H. M. D.

Ionisation and Polymerisation in Cadmium Iodide Solutions. R. G. VAN NAME and W. G. BROWN (*Amer. J. Sci.*, 1917, [iv], **44**, 453—468. Compare A., 1917, ii, 455).—In the further investigation of the constitution of cadmium iodide solutions, measurements have been made of the *E.M.F.* of cells in which iodine electrodes are in contact with iodine–cadmium iodide solutions, and also of the freezing points of solutions containing cadmium iodide and varying proportions of iodine.

The freezing-point data show that the freezing point of a cadmium iodide solution is depressed to the extent of about $1·4°$ per mol. of added iodine. This lowering is very nearly the same for solutions in which the cadmium iodide concentration is varied considerably. The facts point to the existence of polymerised molecules in considerable quantity.

From the *E.M.F.* data it is possible to calculate the iodine ion concentration in iodine–cadmium iodide solutions, and by extrapolation to zero iodine concentration to obtain the iodine ion concentration for pure solutions of cadmium iodide. For the more dilute cadmium iodide solutions examined ($0·01$ and $0·125$ molar) the data are in agreement with the assumption that complex molecules are present, but the behaviour of the stronger solutions does not appear to be compatible with this hypothesis.

The assumption that complex molecules of the type $(CdI_2)_3$ are the only complex molecules formed is found to be insufficient to reconcile the observations which have been made according to the distribution, freezing-point, and *E.M.F.* methods.   H. M. D.

A Comparison of the Activities of Two Typical Electrolytes. G. A. LINHART (*J. Amer. Chem. Soc.*, 1917, **39**, 2601—2605).—Measurements of the *E.M.F.* of cells of the type $H_2|HCl|HgCl|Hg$ have been made for solutions containing from $0·01$ to $16·0$ mols. of hydrogen chloride in 1000 grams of water. From the results, the ionic activities are calculated and compared with the corresponding values for potassium chloride. On the assumption that these thermodynamic quantities afford a measure

of the degree of ionisation of the two electrolytes, it is found that there is a considerable divergence between the degrees of ionisation even in dilute solution, whilst in concentrated solutions the divergence is enormous. H. M. D.

Specific Heats and Heats of Fusion of Triphenylmethane, Anthraquinone, and Anthracene. JOEL H. HILDEBRAND, (MISS) ALICE D. DUSCHAK, A. H. FOSTER, and C. W. BEEBE (*J. Amer. Chem. Soc.*, 1917, **39**, 2293—2297).—The specific heat and latent heat of fusion of triphenylmethane, anthraquinone, and anthracene have been determined in a calorimeter similar to that described by Lewis and Randall (A., 1911, ii, 371). The specific heats were determined over several temperature ranges. The materials were contained in vessels of quartz glass or "pyrex" glass, and consequently the specific heat of these substances had to be determined. The following values were obtained : pyrex glass, $s = 0·174 + 0·00036t$; quartz glass, mean value over the range 20—320°, $s = 0·2161$; triphenylmethane, solid, $s = 0·186 + 0·00277t$, liquid, $s = 0·479$; anthraquinone, solid, $s = 0·258 + 0·0007t$, liquid, $s = 0·66$; anthracene, solid, $s = 0·280 + 0·0007t$, liquid, $s = 0·509$. The following heats of fusion were also obtained : triphenylmethane, 17·8 cal.; anthraquinone, 37·4 cal.; anthracene, 38·7 cal. It is pointed out that the specific heat equation for triphenylmethane is not trustworthy for extrapolation to lower temperatures, as the range of temperature from which it was obtained was so small (20—60°), and it is also suggested that the temperature coefficient of the specific heat is much larger than would be expected.

J. F. S.

The Entropy of the Elements and the Third Law of Thermodynamics. GILBERT N. LEWIS and G. E. GIBSON (*J. Amer. Chem. Soc.*, 1917, **39**, 2554—2581).—A theoretical paper in which the authors have calculated the entropies of the elements and applied the results in testing the theorem of Nernst, which may be regarded as equivalent to the statement that the entropy of every substance is zero at the absolute zero of temperature. On the assumption that the entropy of a substance is known at one temperature, the entropy at any other temperature can be calculated if the specific heat is known for the interval of temperature concerned. It is shown that the entropy may be calculated by a graphical method which does not necessitate any assumption in regard to the exact form of the heat capacity equation. The calculated atomic entropies show with respect to atomic weight or atomic number the same kind of periodicity which characterises certain other properties of the elements.

According to the equation $\Delta F - \Delta H = - T\Delta S$, in which ΔF is the increase in free energy, ΔH the increase in total energy, and ΔS the increase in entropy for any isothermal change, it is possible to calculate the free energy of formation of any compound from its elements if the entropies of the compound and of the elements and

the heat of formation of the compound are known. Conversely, the entropy change associated with the formation of a compound from its elements can be calculated from the equation if the changes in total and free energy are known.

The entropy differences, thus calculated, for a number of compound substances are found to agree satisfactorily with those which are derived from the atomic and molecular entropies, calculated according to the method referred to above, in which it is assumed that the entropies of the elements and compounds are zero at the absolute zero of temperature.

This agreement is considered to afford new support for the so-called third law of thermodynamics.   H. M. D.

Determination of Boiling Points in Capillary Tubes.

FRIEDRICH EMICH (*Monatsh.*, 1917, **38**, 219—223).—An open glass tube 7—8 cm. long, of external diameter 0·6—1·2 mm., and with a wall 0·1 mm. thick, is drawn out at one end to a fine capillary approximately 2 cm. long and of 0·05—0·1 mm. diameter. The end of the capillary is immersed in the liquid to be examined, and when about half a cubic millimetre has entered, the tip is sealed by contact with a flame. If this operation is successful, the capillary will have a minute bubble at the extreme end covered by a liquid plug nearly 1 millimetre in length. The tube is attached to a thermometer and warmed in a bath in which the heating liquid is 4—5 cm. deep. As the temperature is raised, the plug of liquid ascends the capillary, and the b. p. is registered when the plug reaches the level of the surface of the heating liquid outside. The method is, naturally, restricted to pure substances.
                                             D. F. T.

An Efficient Apparatus for Fractional Distillation under Diminished Pressure.

WILLIAM A. NOYES and GLENN S. SKINNER (*J. Amer. Chem. Soc.*, 1917, **39**, 2718—2720).—A modified Claisen flask is used. The side-tube of the flask is bent upwards and fused on to a simple fractionating column, and into the side of the neck of the flask is fused a separating funnel. The flask can thus be used for large or small fractions by regulating the flow of liquid from the separating funnel, and successive fractions may be introduced without losing the vacuum.   W. G.

Studies in Catalysis. VIII. Thermochemical Data and the Quantum Theory. High Temperature Reactions.

WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1917, **111**, 1086—1102. Compare *ibid.*, 457).—According to the radiation theory and the quantum hypothesis, the heat of a reaction Q is given by the equation $Q = Nh(\Sigma v_2 - \Sigma v_1)$, in which N is the Avogadro constant, h the Planck constant, Σv_1 the sum of the critical frequencies of the reacting substances, and Σv_2 the corresponding quantity for the resultant products. This relation has been previously deduced by Haber (*Ber. Deut. physikal. Ges.*, 1911, **13**, 1117), who calculated the

critical frequencies of substances for which the requisite data were not available by means of the semi-empirical relation $v_v/v_r = \sqrt{M/m}$, in which v_v is the characteristic ultra-violet frequency, v_r the characteristic ultra-red frequency in terms of which the specific heat may be represented, M the molecular weight of the substance, and m the mass of an electron. The use of this equation involves considerable uncertainty in regard to M, and in Haber's treatment of the problem in its application to the formation of a salt, such as sodium chloride, from its elements, the quantity Σv_1 is arbitrarily made equal to half the sum of the critical frequencies of the elements instead of the entire sum.

By making the assumption that the ultra-violet quantum breaks the bond between two adjacent atoms, which are both thereby rendered chemically active, it follows that one quantum characteristic of sodium plus one quantum characteristic of chlorine will suffice to bring about the change represented by $2Na + 2Cl = 2NaCl$. Hence, $2Nhv_{NaCl} - Nh(v_{Na} + v_{Cl})$ should be equal to the heat of formation of two gram-molecules of sodium chloride. This relation is identical with that which follows from the introduction of the arbitrary assumption which is characteristic of Haber's method of treatment.

The application of the equation to the calculation of the heat of formation of sodium chloride may be briefly indicated. From the wave-length $(\lambda = 52 \mu)$ of the characteristic infra-red band, $v_r = 0.0577 \times 10^{14}$. By means of the square root relation (see above), $v_v = 19.27 \times 10^{14}$, from which the critical increment $Nhv_{NaCl} = 182,290$ cal. Similarly, the sum of the critical increments for 1 gram atom of sodium and 1 gram atom of chlorine is found to be 85,000 cal. The heat of formation of the salt is therefore $182,290 - 85,000 = 97.290$ cal., which agrees with the observed value, 97,800 cal.

Similar calculations have been made in respect of other substances for which the requisite data are available, and the results, when compared with the observed heats of reaction, show a degree of agreement which supports the validity of the equation connecting the heat of reaction and the critical frequencies.   H. M. D.

Thermochemical Studies. DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii]. **96**, 26—34).—A theoretical paper in extension of the earlier mathematical discussion (A., 1904, ii, 382, 605; 1905, ii, 76, 677) of the heat of formation of carbon compounds, the thermal effect of the intramolecular linkings being especially considered from the author's point of view.   D. F. T.

Thermochemical Studies. The Constitution of Benzene and of some Condensed Aromatic Hydrocarbons considered from the Thermochemical Point of View. DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii], **96**, 35—49).—The relative stability of the cyclic hydrocarbons, containing rings larger than *cyclo*pentane as compared with the smaller rings such as *cyclo*propane, is attributed to the strain in reducing the angle between

the carbon valencies in the latter causing an endothermic effect, whereas, in the author's view, the enlarging of the valency angle in the formation of hexatomic and bigger rings produces an exothermic effect if the ring is a plane one. Mathematical arguments are adduced in favour of this theory, and the annexed formulæ are suggested for benzene, naphthalene, anthracene, and phenanthrene respectively.
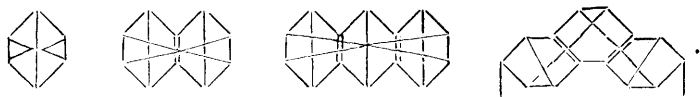
D. F. T.

The Standard Unit in the Thermochemistry of Organic Compounds.
W. SWIENTOSLAWSKI (*J. Amer. Chem. Soc.*, 1917, **39**, 2595—2600).—The values obtained for the heats of combustion of naphthalene, benzoic acid, and sucrose in recent measurements are compared and discussed. In terms of the 15° calorie, the most probable values for the heat of combustion of 1 gram of substance, weighed in air, are: naphthalene, 9612 Cal.; benzoic acid, 6311 Cal.; sucrose, 3945 Cal.

To obtain satisfactory agreement in thermochemical data, it is recommended that the heat capacity of calorimetric bombs should be determined by a standard method involving the use of a standard combustible substance. The question whether the heat of combustion is to be expressed in terms of kilo-joules or calories should be determined by the International Congress. Until the standard substance has been decided on, the calibration of calorimetric bombs should be based on one or other of the above values for the heats of combustion of naphthalene, benzoic acid, or sucrose.

H. M. D.

Improved Form of Pyknometer.
MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1917, **39**, 2387—2388).—A modification in the cap of the side arm of a pyknometer to provide for any liquid which may be driven out of the instrument by expansion during the weighing.

J. F. S.

Improved Victor Meyer Vapour Density Apparatus.
D. A. MacINNES and R. G. KREILING (*J. Amer. Chem. Soc.*, 1917, **39**, 2350—2354).—Improvements to the Victor Meyer vapour density apparatus in connexion (i) with the means of introducing the substance, (ii) with the vaporisation tube, are described. It is pointed out that when the cork of the usual form of the apparatus is withdrawn to allow of the admission of the substance under investigation, there is a certain amount of cooling of the air inside the tube, also there may be a certain amount of spirting of the liquid on to the walls of the vaporisation tube. Both these effects will produce errors. The authors suggest a means of introducing the substance at the bottom of the bulb, and at the temperature of

the vaporisation tube. A long glass tube reaching almost to the bottom of the vaporisation tube is fitted by means of a rubber stopper in the neck of the apparatus. A brass rod, fitted with a hook at its lower end, passes down this tube and is made air-tight at the upper end by means of a rubber tube. The substance under investigation is placed in a small bulb which has a long capillary neck (2—3 cm.) bent twice at right angles. This is placed on the brass hook and the rod drawn up until the bulb neck just touches the enclosing glass tube. When the temperature of the vaporisation vessel is constant, the bulb is broken by drawing the brass rod slightly further up the tube.

It is stated that the air in the ordinary vaporisation tube not being all at the same temperature is the cause of many errors. To obviate these, the authors suggest a modified form of vaporisation vessel. This consists of a large test-tube 25 cm. long and 5 cm. diameter, which carries a rubber stopper, through which passes a capillary delivery tube and a straight tube 28 cm. long and 1·5 cm. diameter. The latter tube is placed centrally, reaches almost to the bottom of the outer vessel, and carries the breaking apparatus described above. The whole apparatus is placed in a large boiling tube in the usual manner. It is to be pointed out that with this apparatus, owing to the sudden rush of air when the tube of material is broken, the usual eudiometer and pneumatic trough are useless, and must be replaced by a gas burette. Trial experiments are described with numerical details for bromine, ethyl alcohol, and diethyl ether. The results are in every way quite good.

J. F. S.

Convergence of the Liquid and Solid Volume Curves to Absolute Zero. GERVAISE LE BAS (*Chem. News*, 1917, **116**, 307—308).—It is shown that, in general, the solid and liquid curves converge to absolute zero. This applies to types of substances where the liquid volume curve is steeper than the solid curve, where the volume of the resultant solid is greater than that of the liquid.

W. P. S.

The Relation between Temperature and Molecular Surface Energy for Liquids between −80° and 1650°. F. M. JAEGER (*Zeitsch. anorg. Chem.*, 1917, **101**, 1—214).—The author has determined the surface tension and molecular surface energy of about 200 organic liquids between −80° and 250°, and of about 50 inorganic substances in the molten condition between 300° and 1650°. The method employed was to determine the bursting pressure of bubbles of the liquid blown on the end of a capillary tube of known diameter just immersed in the liquid. For high-temperature work, the substance under examination was melted in a vessel of platinum or platinum–rhodium heated in a resistance furnace, the capillary tube being of the same material. The complicated apparatus used is described and illustrated in great detail.

In the specially designed manometer, normal octane was used in contact with mercury; it is strongly recommended as an ideal liquid for this purpose.

For each of the substances examined a table is given, in which is detailed, for each temperature at which observations were made, (1) the surface tension χ in ergs per square centimetre, calculated from the equation $\chi = rH/2$, where r is the radius of the capillary and H is the bursting pressure in dynes; (2) the density, d, of the liquid; (3) the molecular surface energy μ in ergs per square centimetre, where $\mu = \chi(M/D)^{\frac{2}{3}}$; (4) the specific cohesion $A^2 = 2\chi/(g \cdot d)$; (5) the quantity $(A^2M)/T$, where T is the absolute temperature of the melting point; (6) the temperature coefficient of the molecular surface energy, $d\mu/dt$. Every substance examined was carefully purified and its density determined at different temperatures, special methods being developed for the high-temperature measurements. For many of the substances χ-t and μ-t curves are given.

It has been demonstrated by Eötvös, from van der Waals's law of corresponding states, that for normal, non-associated liquids $d\mu/dt$ should be a constant $= 2 \cdot 25$ ergs per $1°$, whilst for associated liquids the temperature coefficient should be smaller. Further, it can be shown thermodynamically that if $d\mu/dt$ is a constant, the specific heat of the surface layer must be the same as that of the bulk of the liquid.

The great number of μ-t curves now examined illustrates well the constitutive character of molecular surface energy. The curves are rarely straight lines, the value of the temperature coefficient, in the case of organic liquids, generally falling, but sometimes increasing, with rising temperature. In general, in a series of related substances, such as alcohols, fatty acids, or esters, at a given temperature, the value of μ increases with the molecular weight. The introduction of increasing quantities of halogen into hydrocarbons also increases the molecular surface energy. Isomeric substances, such as ethylene dichloride and ethylidene chloride, show wide differences. The value of $d\mu/dt$ is fairly constant for a series of related substances, but marked exceptions sometimes occur; thus formic acid has an exceptionally low value. In the primary, secondary, and tertiary aliphatic amines, the values of μ and $d\mu/dt$ increase very markedly with increasing carbon content, the lower members of the series having abnormally low temperature coefficients. Of isomeric primary amines, those with straight carbon chains have greater molecular surface energy than those with branched chains. Unsaturated substances, such as allylamine, have higher values of μ than the corresponding saturated compounds. Formamide has an exceptionally low temperature coefficient, $0 \cdot 89$ erg per $1°$, similar to that of water. This fact is probably to be associated with its high dissociating power.

The unsaturated character of aromatic compounds is accompanied by increased values of μ. The halogenated compounds show increasing values of μ with increasing molecular weight. Position isomerides show marked differences; for example, of the three nitro-

phenols, the para-compound has the greatest and the ortho-compound the least molecular surface energy. In the nitroanisoles the differences are much less marked, probably because here there is no mobile hydrogen atom. The molecular surface energy of aniline and its homologues is much higher than that of any of the primary aliphatic amines up to heptylamine. The introduction of halogen or nitro-groups into aniline increases the value of μ, as in the hydrocarbons. The surface energy relationships of many other aromatic compounds are discussed.

Specially interesting are the μ-t curves for such substances as p-azoxyanisole, p-azoxyphenetole, and anisaldazine, which form anisotropic liquids (liquid crystals). The curve consists of two distinct portions with a sharp minimum where the liquid passes from the anisotropic to the normal form. The temperature coefficient of the anisotropic liquid is always greater than that of the normal liquid, a fact which is contrary to Eötvös's conclusion that a lower temperature coefficient indicates a greater degree of molecular association. It is concluded that in substances of this class, very complex and little understood changes are brought about by heat.

The relationships among the haloids of phosphorus, arsenic, antimony, and bismuth are in general similar to those among organic halogen compounds, the values of χ and μ increasing with the molecular weight, whilst the magnitude of $d\mu/dt$ is more or less normal. Quite different, however, are the haloids of the alkali metals lithium, sodium, potassium, rubidium, and cæsium. For the same metal, the surface tension χ of the molten salt decreases with increasing atomic weight of the halogen from fluorine to iodine, and also decreases, for the same halogen, with increasing atomic weight of the metal. The values of μ vary in an irregular manner, whilst $d\mu/dt$ is in all cases abnormally small. Other salts investigated include sulphates, nitrates, borates, molybdates, and tungstates of the alkali metals.

It is concluded that at high temperatures the law of corresponding states cannot hold for molten salts, which are probably highly ionised, and that Eötvös's rule, based on the validity of this assumption, that a low value of $d\mu/dt$ indicates a high degree of association in the liquid, is therefore invalid. Also, since $d\mu/dt$ is by no means constant for organic or inorganic liquids, the specific heat of the surface layer must be different from that of the rest of the liquid, and the surface energy must be, at least in part, of a kinetic nature.

The author has investigated the empirical rule, discovered by Walden, that for many non-associated liquids the quotient obtained by dividing the molecular cohesion by the absolute temperature of (a) the melting point or (b) the boiling point is a constant, in the case of (a) 3·65 and of (b) 1·15 approx. The values of these two "constants" have been calculated and tabulated by the author for about 200 different substances, which are divided into four groups according to the manner in which either value varies from

the mean. The rule is evidently only approximate, and many variations occur which cannot be explained on the ground of molecular association. The greatest irregularities occur, however, among inorganic salts.   E. H. R.

Solubility and Internal Pressure. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1917, **39**, 2297—2301. Compare A., 1916, ii, 518).—Where Raoult's law is obeyed by a solution, the solubility of the solid at the absolute temperature T may be calculated by means of the expression $\log N = -LTT_m/4\cdot58(T_m - T)$, where N is the solubility expressed in terms of molecular fractions, L is the molecular heat of fusion, and T_m the melting point in absolute degrees. The author has calculated the solubility of anthracene, anthraquinone, p-dibromobenzene, phenanthrene, and triphenylmethane at 25° by means of the formula, and compared these values with the experimentally determined solubilities (see this vol., i, 62) in some eight solvents. Iodine has been treated similarly. The divergence of the solubility from the calculated value is considered along with the internal pressure of the solvent, and it is shown in the case of anthracene, which has practically the calculated solubility in carbon disulphide, that its solubility decreases with decreasing internal pressure for non-polar liquids. In the case of alcohol, a polar liquid, the divergence from the calculated solubility is much greater, a fact which agrees with the third rule previously stated (*loc. cit.*).   J. F. S.

Formation of Additive Compounds in Aqueous Solutions. Stability of Hydrates and the Determination of Hydration in Solution. JAMES KENDALL, JAMES ELIOT BOOGE, and JAMES C. ANDREWS (*J. Amer. Chem. Soc.*, 1917, **39**, 2303—2323).—The results of previous work on the formation of additive compounds are summarised, and the general rules established in this work are recapitulated and extended to aqueous solution (A., 1914, i, 858, 1069; 1915, i, 15, 80; 1916, i, 599, 707). Since water can function both as a weak acid and a weak base, the extent of hydration in aqueous solutions should be found to increase with the increasing acidity or basicity of the solute. The known hydrates of acids and bases are reviewed in the paper, and it is shown that only the stronger acids and bases yield compounds with water which are capable of isolation. A number of freezing-point determinations with solutions of varying concentrations of the following acids, acetic, β-hydroxypropionic, α-hydroxypropionic, citric, d-tartaric, hydrofluoric, phosphoric, and hydrochloric, have been carried out. The results in all cases conform exactly with the above-mentioned prediction. A critical discussion is given of the factors which must be taken into consideration in the determination of hydration in solution by the freezing-point method. The question of the hydration of salts is treated in a preliminary manner, and it is shown that the hydration follows the order of the scheme
$$\text{Ce} < \text{Rb} < \text{K} < \text{NH}_4 < \text{Na} < \text{Li}$$
and $\text{NO}_3 < \text{Cl} < \text{Br} < \text{I}$.   J. F. S.
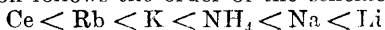
Mechanism of the Ionisation Process. JAMES KENDALL
and JAMES ELIOT BOOGE (*J. Amer. Chem. Soc.*, 1917, **39**,
2323—2333).—The results of a number of papers by the authors
(see preceding abstract) have indicated an intimate and general
connexion between ionisation and the formation of compounds in
solution. In the present paper the authors advance the hypothesis
that ionisation is preceded by combination between solvent and
solute, and is, indeed, a consequence of such combination. This
point of view combines the current ionic and hydrate hypotheses, re-
ferring conductivity in solutions to the dissociation of solute–solvent
complexes into radicles of opposite charge. The actual mechanism
of the ionisation process under this assumption, with its relation to
phenomena such as unsaturation, association, and high dielectric
constant, is briefly discussed. It is shown that compound forma-
tion between solvent and solute may be postulated in all conduct-
ing solutions, and that the distinction still commonly retained
between the two components is arbitrary and misleading. The
general evidence in favour of the hypothesis is given in a pre-
liminary form, attention being centred on a few fundamental points
only.   J. F. S.

Soap Bubbles as Models of Crystal Structure. M. J.
MARSHALL (*J. Amer. Chem. Soc.*, 1917, **39**, 2386—2387).—It is
shown that when small soap bubbles of uniform size are produced
on the surface of a soap solution, they form a symmetrical network
which is in reality the simple face-centred lattice as found in
crystals of pure metals. These bubble aggregates can readily be
produced and projected on the screen, and so serve to show causes
of crystal structure and the method of building up of crystals. The
best effects are produced by using a solution of sodium oleate to
which glycerol has been added, and blowing the bubbles by means
of a glass tube which has been constricted to 1 mm. diameter by
drawing, and then further constricted to a very fine tip by allow-
ing the walls of the 1 mm. tube to fall together in a smoky flame.
The jet should be at right angles to the surface of the soap solution
when the bubbles are blown.   J. F. S.

Formation of Crystals in Gels. HARRY N. HOLMES (*J.
Physical Chem.*, 1917, **21**, 709—733).—The influence of silicic acid
gels on the formation of crystals has been examined by experiments
in which one of two reacting soluble substances was added to a
solution of silicic acid, which was then allowed to set. The second
substance, dissolved in water to give a solution having a greater
osmotic pressure than the jelly, was then brought into contact with
the upper surface of the jelly and slow diffusion allowed to take
place. If an insoluble substance is produced by the reaction, this
forms within the jelly, and the slow diffusion process leads to the
formation of large, well-developed crystals. Perfectly formed tetra-
hedral crystals of copper may, for instance, be obtained by the
diffusion of hydroxylamine hydrochloride into a silicic acid gel con-

taining copper sulphate. Other substances obtained in crystalline form by this method were silver dichromate, gold, lead iodide, mercuric iodide, basic mercuric chloride, silver sulphate, silver acetate, and basic lead chromate.

The capillarity associated with the gel structure is supposed to be partly responsible for the observed crystal growth, and a similar influence is brought into play when the fine-grained precipitation membrane begins to be formed. In support of the theory that the capillary diffusion is the chief factor in the phenomenon, it has been observed that well-formed crystals may be obtained by allowing slow diffusion to take place through flowers of sulphur, barium sulphate, or alundum.   H. M. D.

Properties of Mixed Liquids. III. Law of Mixtures. I. J. Livingston R. Morgan and Mary A. Griggs (*J. Amer. Chem. Soc.*, 1917, **39**, 2261—2275. Compare A., 1916, ii, 224, 296).— With the object of testing the validity or otherwise of the simple law of mixtures, the surface tension of a number of homogeneous mixtures has been determined by the drop-weight method at two temperatures in each case. The lower temperature was 10° or 15° and the higher temperature 40°. The following mixtures in a series of compositions were measured : (*a*) Binary mixtures : benzene–toluene, benzene–ethyl propionate, benzene–chlorobenzene, benzene–methyl butyrate, benzene–propyl acetate, benzene–acetone, toluene–ethyl propionate, toluene–chlorobenzene, toluene–methyl propionate, toluene–ethyl formate, acetone–chlorobenzene, chlorobenzene–ethyl propionate, ethyl lactate–propyl acetate, chlorobenzene–methyl butyrate, amyl β-phenylpropionate–methyl propionate, and acetone–propyl acetate. (*b*) Ternary mixtures : benzene–toluene–ethyl propionate, benzene–toluene–chlorobenzene, benzene–toluene–methyl propionate, and benzene–toluene–acetone. (*c*) Quaternary mixtures : benzene–toluene–ethyl propionate–chlorobenzene, benzene–toluene–methyl propionate–ethyl lactate, and benzene–toluene–methyl butyrate–propyl acetate. (*d*) Quinary mixture : benzene–toluene–methyl butyrate–propyl acetate–methyl propionate. It is shown that ten of the above-mentioned mixtures follow rigidly the law of mixtures in the form $P_{Mixt.} = l_a P_a + l_b P_b + $, etc. (where the summation of the relative weights l_a, l_b, etc., is equal to unity. Of these mixtures, six were of two constituents, two of three constituents, one of four constituents, and one of five constituents. Where variations appear, the observed value is invariably less than that calculated from the law. These deviations increase in magnitude with increased temperature, and are always at a maximum at both temperatures for that mixture which contains equal weights of the constituents. Although the deviations might be due to the magnitude of the difference in the surface tension values of the constituents when pure, the effect is probably negligible and merges into the more important factor—the nature of the constituent. An example of the latter is chlorobenzene, which renders every mixture in which it is present abnormal. The deviation of a complex mix-

ture is not a summation of the deviations of the pairs of liquids of which it could be made, but is of the same order as these. It is further shown that chemical interaction for binary mixtures could not be the cause of the maximum deviation invariably found at a composition of 50% by weight of the two constituents, whereas this behaviour is shown to be exactly what might be expected if the one liquid by its simple, physical presence influenced the value of the property of the other, and the conclusion is consequently drawn that the mixture law considered is a rigid law provided no chemical action takes place between the constituents and neither liquid influences the value of the property of the other.   J. F. S.

Properties of Mixed Liquids. IV. Law of Mixtures. II. J. LIVINGSTON R. MORGAN and ANDREW J. SCARLETT, jun. (*J. Amer. Chem. Soc.*, 1917, **39**, 2275—2293. Compare preceding abstract).—The surface tension of the following binary mixtures, (i) water–acetone, (ii) acetone–ethyl alcohol, (iii) phenol–acetone, (iv) phenol–ethyl alcohol, (v) benzene–acetic acid, (vi) benzene–ethyl alcohol, (vii) benzene–methyl alcohol, (viii) acetone–methyl alcohol, (ix) ethyl alcohol–methyl alcohol, and (x) benzene–phenol, has been determined by the drop-weight method over a range of concentrations and temperatures. The curves representing the variation in surface tension with concentration are in general without maxima or minima, but that of (v) shows a minimum, whilst (ii) and (viii) show maxima. The comparison of the experimental results with those calculated by means of the mixture law of Morgan and Griggs leads to the following observations, which fall into three groups: (*a*) the systems (i), (iii), (iv), (v), (vi), (vii), and (x) give values smaller than the calculated values; (*b*) systems (ii) and (viii) give values larger than the calculated values; (*c*) the remaining system, (ix), gives a slight positive deviation at 0°, no deviation at 30°, and a slight negative deviation at 45°.

The position and magnitude of the maximum deviation, from the mixture law, found when the deviation is plotted against the concentration of one constituent, divides the systems into two classes. In one class the maximum deviation, always very small, is found for a mixture containing 50% by weight of each constituent. The systems falling into this group are (ii), (viii), and (ix). The only explanation of this behaviour is that it is due to the physical effect of the one liquid on the other, since an equal weight of the two constituents brings about the effect.

Systems of the other class, on the contrary, exhibit a maximum deviation, usually large, and at some other concentration than 50% which corresponds always with some simple and even relation of the molecular weights of the constituents, that is, corresponds with a definite chemical formula. The cause of this, according to the theory put forward by Denison (A., 1913, ii, 30), is the actual production of a compound. The molecular compounds found to exist in the binary mixtures of liquids examined are: $COMe_2,10H_2O$, $2PhOH,COMe_2$, $PhOH,2EtOH$, $C_6H_6,2CH_3\cdot CO_2H$,

$2C_6H_6$,EtOH, C_6H_6,MeOH, and 4PhOH,$3C_6H_6$.   The existence of these compounds in solution is confirmed by density and viscosity measurements.   The compound C_6H_6,$2CH_3\cdot CO_2H$ shown to exist in the system benzene–acetic acid is particularly interesting when considered in the light of the results of other methods, which lead to the conclusion that acetic acid is always polymerised into double molecules in benzene solution.   These methods are such, however, as would fail to show a combination of the solvent with the polymerised solute, even if it did exist; and hence the evidence found here is not only not inconsistent with other evidence, but gives a wider point of view on the process which has been designated hitherto as a simple polymerisation.   J. F. S.

System of Recording Rate of Chemical Reaction. JAMES W. McBAIN (*Chem. News*, 1917, **116**, 315—316).—It is suggested that the usual expression for denoting the velocity constant of a reaction may be replaced by a number which has a direct physical significance.   For instance, it may be written $k=1/t$ (remainder of the expression), where k is the present rate constant of the reaction and t is the time the reaction has proceeded, or $kt=$ (remainder of the expression).   It is necessary to give the value of k and also the value of the unit of time (minutes or hours).   The value of k is, however, always set at unity, and the unit of time is chosen accordingly; the equation then becomes $t=$ (remainder of the expression).   The chief advantage is that the proposed "unit of time" gives a direct idea of the rate of the reaction.   W. P. S.

Contact Catalysis. III. WILDER D. BANCROFT (*J. Physical Chem.*, 1917, **21**, 734—775.   Compare A., 1917, ii, 566; this vol., ii, 13).—A review of the literature relating to the action of poisons in contact catalytic reactions.   The changes in over-voltage produced by certain ions are supposed to be effects which are comparable with retarded or inhibited contact catalytic reactions.
    H. M. D.

Revision of Atomic Weights in 1916. E. MOLES (*J. Chim. phys.*, 1917, **15**, 433—469).—A review of the work on the determination of atomic weights published during 1916.   H. M. D.

Errors affecting the Determination of Atomic Weights. VI. Surface Actions as a Source of Errors in Weighing. PH. A. GUYE and E. MOLES (*J. Chim. phys.*, 1917, **15**, 360—404. Compare A., 1916, ii, 385, 386, 432, 445).—A further consideration of the errors involved in the accurate determination of equivalent weights, in which the authors direct attention to the anomaly, first pointed out by Hinrichs (compare A., 1893, ii, 163, 316; 1894, ii, 276), that the value of the combining ratio is a function of the quantity of substance used in the determinations.   It is considered that the available data afford clear evidence that such a relation does actually exist, but the interpretation given by Hinrichs is considered to be unacceptable.

By reference to data obtained in recent work on the determination of atomic weights, it is found that all series of measurements do not show the occurrence of such a connexion between the combining ratio and the quantity of substance operated on, but that this is confined to series of determinations in which the quantities of substance employed have been determined by weighing in air, the reduction to a vacuum being effected by calculation. This suggests that the anomaly is due to surface condensation of air, water, etc., and it is shown that the curves which express the relation between the experimental combining ratio and the weight of substance operated on can be satisfactorily accounted for on this hypothesis. The average relative deviation attributable to this source of error is 1 in 20,000, but it is sometimes as high as 1 in 10,000. H. M. D.

Errors affecting the Determination of Atomic Weights. VII. Surface Actions as a Source of Errors in Weighing. Ph. A. Guye and E. Moles (*J. Chim. phys.*, 1917, **15**, 405—432. Compare preceding abstract).—Experiments have been made with silver in the form of a solid block and with finely powdered zinc oxide with the object of ascertaining the magnitude of the errors which may be ascribed to the formation of a surface film when these substances are weighed in the air. In the case of silver, the error involved amounts to 2×10^{-5} gram per gram of silver. This value is to be regarded as a minimum, the actual error in practice depending on the humidity of the air in the balance case, on the nature of the surface of the metal, and on other factors. The error attributable to surface condensation, according to the experiments with zinc oxide, is of the order 0.2 to 0.4×10^{-5} gram per gram of substance.

It is shown that errors of this order of magnitude affect the value of the second decimal figure when the atomic weight of the element under consideration is greater than 100. The errors in question should be eliminated in atomic weight measurements by actually weighing the substances involved in a vacuum. The possibility of making such weighings has been greatly increased as a result of recent improvements in the technique of various forms of microbalance. H. M. D.

Graphical Interpolation of Tabulated Data. Horace G. Deming (*J. Amer. Chem. Soc.*, 1917, **39**, 2388—2392).—A method is described, based on the principle of a triple parallel alignment chart, whereby the interpolated values required from data may be rapidly obtained by a graphic method. It is claimed, for example, that the adoption of this principle to logarithm tables would reduce the amount of space occupied by such tables to about 10% of that now necessary. J. F. S.

Inorganic Chemistry.

Revision of the Atomic Weight of Bromine. Normal Density of Hydrogen Bromide Gas. CLARENCE KENWORTHY REIMAN (*J. Chim. phys.*, 1917, **15**, 293—333).—A full account of work already published (compare A., 1917, ii, 137, 200).

H. M. D.

Revision of the Atomic Weight of Bromine. Normal Density of Hydrogen Bromide Gas. WALLACE JENNINGS MURRAY (*J. Chim. phys.*, 1917, **15**, 334—359).—A full account of work previously published (A., 1917, ii, 201).   H. M. D.

Chemical Reactions in the Corona. I. Ozone Formation. F. O. ANDEREGG (*J. Amer. Chem. Soc.*, 1917, **39**, 2581—2595).—An account is given of some preliminary observations which have been made on the formation of ozone during the passage of a current of oxygen through a tube in which corona discharge is maintained. The results suggest that a condition of equilibrium is rapidly attained. It is hoped that the study of this and other reactions in the corona discharge will throw some light on the connexion between ionisation and chemical reaction.   H. M. D.

Analytical Control of the Ammonia Oxidation Process. G. B. TAYLOR and J. D. DAVIS (*J. Ind. Eng. Chem.*, 1917, **9**, 1106—1110).—In the catalytic oxidation of ammonia by means of atmospheric oxygen for the production of nitric acid, the following reactions take place:

$$4NH_3 + 5O_2 = 4NO + 6H_2O \quad . \quad . \quad . \quad . \quad (1)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O \quad \quad . \quad . \quad . \quad (2)$$
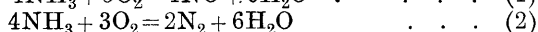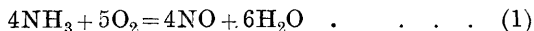
and the possibility of the second reaction being produced by means of an intermediate reaction,

$$4NH_3 + 6NO = 5N_2 + 6H_2O \quad . \quad . \quad . \quad . \quad (3)$$

was pointed out by Reinders and Cats (A., 1912, ii, 248). Evidence that this third reaction does take place under certain conditions has been obtained in the case of a badly constructed oxidiser, in which irregular cooling of the catalyst was produced locally by currents of the burned gases. Samples taken from points near the cool places contained ammonia, whereas in samples taken outside the catalyst chamber the proportion of ammonia was low. It was probable that most of this ammonia passing such points was subsequently "burned" by the hot nitric oxide. Effective working in a converter depends on maintaining conditions which promote reaction (1) and are unfavourable to reaction (2). [See further *J. Soc. Chem. Ind.*, 1918, **37**, 54A.]

C. A. M.

The Solubility of Silica. VICTOR LENHER and HENRY BALDWIN MERRILL (*J. Amer. Chem. Soc.*, 1917, **39**, 2630—2638).—The solubility of silica in water and in aqueous solutions of hydrochloric and sulphuric acids of varying concentration has been measured at 25° and 90°. With gelatinous silica, a condition of equilibrium is reached after a few hours or days, but with ignited silica much longer periods are required for the attainment of saturation. The results seem to show that the solubility of gelatinous silica is independent of the method of preparation of the substance, and that ignited silica will give solutions of the same concentration when the equilibrium condition is reached.

The solubility increases with the temperature, and at a given temperature decreases with increase in the concentration of the acid. Carbon dioxide has no measurable influence on the solubility of silica. The results are not only of interest in connexion with the estimation of silica, but possess considerable geological significance.   H. M. D.

Polysulphides of the Alkali Metals. III. Solidifying Points of the Systems, Sodium Monosulphide–Sulphur, and Potassium Monosulphide–Sulphur. JOHN SMEATH THOMAS and ALEXANDER RULE (T., 1917, **111**, 1063—1085. Compare T., 1914, **105**, 177, 2819).—The freezing-point curves for mixtures of sulphur with sodium monosulphide and potassium monosulphide, derived from observations on the rate of cooling of the mixtures in a current of dry nitrogen, show the existence of a complete series of compounds of the formula R_2S_x, where x is a whole number having the maximum value 5 in the sodium series and 6 in the potassium series.

The members of the potassium series of compounds resemble closely the corresponding rubidium and cæsium compounds (Biltz and Wilke-Dörfurt, A., 1905, ii, 162; 1906, ii, 283, 611), but the sodium compounds differ from their analogues in appearance and properties. This difference is also shown in the comparative stabilities of compounds of corresponding composition and in the maximum combining power of the metals.

The rate at which the polysulphides lose sulphur when heated in a steady stream of hydrogen at regularly increasing temperatures has also been examined. The results obtained indicate that the disulphides of both metals are very stable compounds from which sulphur can only be removed with difficulty at 700—800°. This suggests that the polysulphide molecules contain two atoms of sulphur which are combined differently from the remaining atoms of sulphur. The disulphides are represented by the formula R·S·S·R, and the higher polysulphides by formulæ, such as

$$\overset{S}{\underset{\cdot\cdot}{R\cdot S\cdot S\cdot R}} \quad \text{and} \quad \overset{S\ \ S}{\underset{\cdot\cdot\ \cdot\cdot}{R\cdot S\cdot S\cdot R}} \ .$$
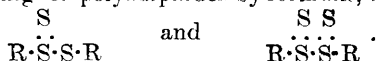
Molecular weight determinations by the boiling-point method in ethyl alcohol solution gave numbers less than those required by the

formula R_2S_x. These results favour the simple formula R_2S_x, as opposed to the doubled formula R_4S_x suggested by Bloxam (T., 1900, **77**, 753). The difference between the actual results and those required by the formula R_2S_x are attributed to ionisation.

No evidence of intermediate compounds, such as the enneasulphides (Bloxam, *loc. cit.*), has been obtained in either series.

H. M. D.

Ammoniacal Copper–Mercury Derivatives.   F. ANDERLINI (*Gazzetta*, 1917, **47**, ii, 171—176. Compare A., 1912, ii, 764).— The *compound*, $CuHgBr_4,4NH_3$, is obtained in dark blue crystals by mixing boiling solutions of ammoniacal cupric bromide and mercury bromide dissolved in potassium bromide. If this compound is dissolved in a warm solution of ammonium bromide and the solution treated with mercury bromide dissolved in potassium bromide, free ammonia being present, but not in excess, the *compound*, $CuHg_2Br_6,4NH_3$, is obtained in bright blue scales or needles.

R. V. S.

Observations on the Rare Earths.   IV.   The Purification of Gadolinium.   LOUIS JORDAN and B. SMITH HOPKINS (*J. Amer. Chem. Soc.*, 1917, **39**, 2614—2623).—The results of experiments are described in which the attempt has been made to separate gadolinium from rare earth mixtures by the fractional precipitation of the dimethyl phosphates, bromates, and glycollates.

Fractionation of the dimethyl phosphates rapidly removes europium and samarium completely, and gadolinium of considerable purity is obtained from the middle fractions. The terbium which is present in this material can be removed by fractionation of the bromates. The glycollate method rapidly removes samarium from gadolinium, but has little effect on the removal of terbium.

The method recommended for the separation of gadolinium from rare earth mixtures is first to remove cerium by the bromate method and fractionally crystallise the residue. The less soluble fractions contain only europium, samarium, gadolinium, and neodymium, which are converted into the dimethyl phosphates and again fractionated. The least soluble fractions will then consist of high-grade gadolinium. Any remaining traces of samarium can be removed by precipitation with sodium glycollate.   H. M. D.

Revision of the Atomic Weight of Samarium.   Analysis of Samarium Chloride.   O. J. STEWART and C. JAMES (*J. Amer. Chem. Soc.*, 1917, **39**, 2605—2614).—A fractionation method for the extraction of samarium from its admixtures with the other rare earth metals is described. The pure samarium oxide was converted into the chloride, $SaCl_3,6H_2O$, which was dried, finely powdered, and heated below 100° until most of the water of crystallisation had been driven off. The temperature was then raised to 180°, and finally to 300°, the tube being traversed by a current of dry

hydrogen chloride. The anhydrous salt was then removed, finely powdered, and heated to its melting point in contact with hydrogen chloride, which was then displaced by nitrogen and finally by air. The atomic weight of the samarium was derived from the ratio $SaCl_3 : 3Ag$. A series of preliminary experiments in which the individual results were not in good agreement gave a mean value $Sa = 150 \cdot 45$, and a final series of eight determinations in close agreement gave a mean value $Sa = 150 \cdot 43$. H. M. D.

Precipitation, Stability, and Constitution of Hydrated Ferric Oxide Sols. I.

MARKS NEIDLE (*J. Amer. Chem. Soc.*, 1917, **39**, 2334—2350).—A systematic study of the precipitation of hydrated ferric oxide sols of varying purity and concentration by means of potassium sulphate. The sols were prepared by oxidising a solution of ferrous chloride containing 1 gram equivalent of ferrous chloride in 400 c.c. of solution by means of 3% hydrogen peroxide. The solutions were then dialysed and diluted to the required concentrations. The content of iron and chlorine was estimated, and the relative stability determined by measuring the volume of a standard solution ($M/800$ or $M/1600$) of potassium sulphate required to effect complete precipitation of the sol. A number of series of such clear sols were prepared, and in each series the iron content was constant, whilst the chlorine content varied. The results show that for a given iron concentration the stability increases with the chlorine concentration, whilst for sols of given purity, that is, for sols which have the same ratio, Fe/Cl, the stability decreases as the concentration increases, this being most pronounced in very pure sols. It is shown that the maximum purity of a sol may be ascertained by graphic extrapolation. A general discussion is given of the results of Nicolardot and Duclaux (A., 1905, ii, 167; 1906, ii, 677). The author advances a chemical theory of the constitution of hydrated ferric oxide sols to explain the relationship between stability and composition. J. F. S.

A New Oxychloride of Tin.

HARRY F. KELLER (*J. Amer. Chem. Soc.*, 1917, **39**, 2354—2356).—During the examination of metallic objects found in the aboriginal cemetery on Hogtown Bayou, Santa Rosa County, Florida, the author noticed a number of cavities, in a piece of tin, which were lined with small, shining crystals. The crystals were mostly in the form of thin plates, but some were acicular. On heating, the substance melts and gives off acrid fumes which form a white sublimate without a trace of moisture. Analysis of a small quantity of the material leads to a composition corresponding with the formula $SnCl_2,SnO$. [See also *J. Soc. Chem. Ind.*, 1918, **37**, 29A.] J. F. S.

Solubility of Bismuth Oxychloride in Hydrochloric Acid and its Relation to Complex Formation.

ARTHUR A. NOYES, FRANK W. HALL, and JAMES A. BEATTIE (*J. Amer. Chem. Soc.*, 1917, **39**, 2526—2532).—The electrical conductivity of a solution

of hydrochloric acid is diminished by the addition of bismuth chloride. The observed diminution can be most satisfactorily interpreted on the assumption that chlorobismuthic acid of the formula H_2BiCl_5 is formed.

Measurements of the solubility of bismuth oxychloride in hydrochloric acid solutions of varying concentration at 25° afford support for this hypothesis in the case of the more concentrated solutions, whilst for the less concentrated acid solutions the solubility data suggest that the predominant complex acid has the formula $HBiCl_4$.   H. M. D.

Mineralogical Chemistry.

Crystal Structure of Copper Pyrites determined by X-Rays.
CHARLES L. BURDICK and JAMES H. ELLIS (*J. Amer. Chem. Soc.*,
1917, **39**, 2518—2525).—The *X*-ray interference effects obtained
with a crystal of copper pyrites ($CuFeS_2$) show that the iron and
copper atoms together form a face-centred tetragonal lattice, the
planes perpendicular to the tetragonal axis consisting of alternate
layers of copper atoms and iron atoms. The sulphur atoms are
located on an exactly similar face-centred lattice, the planes of
sulphur atoms being situated at equal distances from the planes of
iron and of copper atoms in each of the three axial directions.

The density of copper pyrites, calculated from the weights of the
atoms and the distances between the atom planes, is 4·24, whilst
the observed densities recorded in the literature lie between 4·1 and
4·3.   H. M. D.

Tungstenite, a New Mineral. R. C. WELLS and B. S. BUTLER
(*J. Washington Acad. Sci.*, 1917, **7**, 596—599).—This mineral, a
tungsten sulphide, probably WS_2, occurs intimately intermixed with
other minerals in a compact ore from the Emma mine in the Little
Cottonwood district, Salt Lake Co., Utah. Under the microscope,
it is seen as feathery flakes resembling graphite in appearance. It
is lead-grey and opaque with metallic lustre, and soft enough to
mark paper. D about 7·4 (calculated from 6·43 of the specimen
analysed, allowing for impurities). The mineral is unattacked by
hydrochloric or nitric acid, but is decomposed by aqua regia. It
is not oxidised by roasting in air. A bulk analysis of the ore gave:

W.	S.	Fe.	Zn.	Mn.	Ni.	Pb.	As.	Sb.	Cu.	Ag.	SiO$_2$.	H$_2$O.	Total.
44·7	29·1	8·8	0·4	0·6	0·3	4·1	1·0	0·8	1·3	0·4	0·3	0·7	92·5

corresponding with WS_2, 61·5; pyrites, 17·3; tennantite and tetra-
hedrite, 8·1; galena, 4·7%. In chemical composition and physical
characters the mineral is analogous to molybdenite (MoS_2).
                                                       L. J. S.

The Photographic Spectra of Meteorites. SIR WILLIAM
CROOKES (*Phil. Trans.*, 1917, [*A*], **217**, 411—430).—See this vol.,
ii, 25.

Analytical Chemistry.

Gas Interferometer Calibration. JUNIUS DAVID EDWARDS (*J. Amer. Chem. Soc.*, 1917, **39**, 2382—2385).—A simple method of calibrating a Rayleigh-Zeiss gas interferometer is described. This differs mainly from the older method of using two gases of different refractive indices in using dry air free from carbon dioxide in both sides of the apparatus and changing the pressure of one side.

J. F. S.

The Direct Determination of the Hygroscopic Coefficient. FREDERICK J. ALWAY, MILLARD A. KLINE, and GUY R. McDOLE (*J. Agric. Research*, 1917, **11**, 147—165).—An investigation of Hilgard's method for the determination of the hygroscopic coefficient of soils (compare U.S. Dept. Agric. Div., *Chem. Bull.*, 1893, **38**). If carried out exactly as described, it gives trustworthy results, but it is more convenient to replace the sheets of glazed paper by shallow aluminium or copper trays. The absorption boxes must not be increased in size, and a larger number of samples must not be exposed in one box. The hygroscopic coefficient increases with rise in temperature (compare Lipman and Sharp, A., 1912, ii, 84). Preliminary drying of soils at 100—110° does not affect their hygroscopicity, and soils may be ground in steel mortars to pass through a 1 mm. sieve without affecting this coefficient. It is preferable to expose the soil for twenty-four rather than for twelve hours, and it is essential to use only a very shallow layer of soil. Transference of the exposed soil from the boxes to weighing bottles must be performed rapidly, or the results obtained will be too low. W. G.

Estimation of Sulphur in Urine. H. J. HAMBURGER (*Zeitsch. physiol. Chem.*, 1917, **100**, 221—240. Compare A., 1916, ii, 641). —Application of the method previously described to the estimation of inorganic and ethereal sulphate and of neutral sulphur in urine.

H. W. B.

Gravimetric Estimation of Sulphuric Acid and Barium as Barium Sulphate. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1917, **56**, 417—439. Compare *J. Soc. Chem. Ind.*, 1918, **37**, Feb.). —An investigation of the influence of various substances on the precipitation of barium sulphate. Low results are obtained when a large excess of barium chloride is added, but when hydrochloric acid or nitric acid is also present, the results are too high. Potassium salts cause the results to be low unless hydrochloric acid is also present, when they become too high; hydrochloric acid, however, increases the low results obtained in the presence of both potassium chloride and potassium sulphate. Sodium, ammonium, zinc, magnesium, and aluminium chlorides have no effect on the

precipitation, ferric chloride makes the figures for the barium
sulphate to be about 3% too low, and chromium chloride has a
similar effect.   W. P. S.

**Estimation of Nitrogen in Explosives of the Type of
Nitric Esters.** BERNARDO ODDO (*Gazzetta*, 1917, **47**, ii, 145—158).
—In the method of estimation here described, the reaction between
nitrates, sulphuric acid, and mercury is employed, but the process
is made gravimetric instead of volumetric. The explosive is dis-
solved in sulphuric acid in a small conical flask in which a small
test-tube containing the mercury is placed. The flask is closed with
a rubber stopper which carries an inlet tube and (as an outlet) a
U-tube containing sulphuric acid. Purified carbon dioxide is passed
through until all air is displaced (about forty minutes). The
apparatus is then disconnected from the gas supply, closed at each
end with a short rubber tube and glass rod, and weighed. The end
of the U-tube is then opened, the mercury is poured into the flask
by inclining the latter, and the whole is shaken for a few minutes.
When the reaction is complete, carbon dioxide is passed as before.
After reweighing, the percentage of nitrogen can be calculated from
the loss in weight. The results are satisfactory.   R. V. S.

Estimation of Metallic Iron in Ferrum Reductum.
AUGUST EBERHARD (*Arch. Pharm.*, 1917, **255**, 357—381).—Ferrum
reductum used to be prepared by means of pure hydrogen at a not
too high temperature, genuine ferrum hydrogenio reductum being
thereby obtained. In recent years, however, impure hydrogen (con-
taining carbon monoxide) and higher temperatures have been
employed, and these changes have so altered the quality and purity
of the product that the old methods of estimating the iron, par-
ticularly the iodometric methods, no longer yield trustworthy
results.

For the technical method recommended, see *J. Soc. Chem. Ind.*,
1918, **37**, 39A.   C. S.

**Iso- and Heteropoly-acids. XV.   Analytic and Synthetic
Methods for the Investigation of Heteropoly-acids.** ARTHUR
ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1917,
101, 215—224).—A critical summary is given, with numerous
references, of the analytical methods employed for these acids, in-
cluding estimations of water, boric acid, silica, phosphoric, arsenic,
molybdic, and tungstic acids and alkalis. A short outline of the
general methods for preparing heteropoly-acids and salts is also
given.   E. H. R.

General and Physical Chemistry.

Refractivity of Unsaturated Compounds. I. Gervaise Le Bas (*Trans. Faraday Soc.*, 1917, **13**, 53—60).—A discussion of the influence on refractive power of the ethylene and acetylene linkings, of the carbonyl group, and of conjugated carbonyl groups, and of the refractivities of nitrites, nitrates, and oximino-compounds. H. M. D.

The Line Spectrum of Titanium and its Applications. A. de Gramont (*Compt. rend.*, 1918, **166**, 94—99).—A study of the line spectrum of titanium, when fused in the form of its oxide with lithium, sodium, or potassium carbonate and submitted to the action of a condensed spark, or with the direct spark between two fragments of steel containing titanium. The spectrophotographs are reproduced in the original, together with tables showing the rays more sensitive to the eye than to a photographic plate, and those capable of being photographed. The author suggests that the approximate amount of titanium in a steel may be determined by observing which of the titanium rays can be detected. In a similar manner, this method may be used for the examination of minerals. W. G.

The Application of the Quantum Hypothesis to Photochemistry. E. Warburg (*Naturwiss.*, 1917, **5**, 489—494; from *Chem. Zentr.*, 1917, ii, 587—588).—Restricting the term photochemistry to such reactions as do not yield electric end-products, it is probable that the photochemical process does not involve the separation of electrons, because gases undergoing a photochemical change do not exhibit conductivity. It is necessary to distinguish between chemical processes produced directly by the influence of light and secondary reactions. Only those rays which are absorbed exert photochemical action, and the effect is proportional to the absorbed radiation; the chemical change caused by an absorption of radiation equivalent to one gram-calorie is termed the "specific photochemical effect." The hypothesis that photochemical absorption occurs by quanta explains the concentration of the effect on relatively few molecules and accounts for the greater activity of the shorter wave-lengths, the effect being due to an increase in temperature of individual molecules. From the quantum hypothesis, it follows that a molecule, for example, of hydrogen bromide, can be directly decomposed by radiation only if $2c/\lambda > q$, where c is a constant, λ the wave-length, and q the heat effect in gram-calories per molecular weight on recombination of the decomposition products. The apparent contradiction that photolysis can occur with ammonia for wave-lengths of $\lambda = 0.209$, in which case $2c/\lambda < q$, is explained by the possibility that a molecule of ammonia after absorption of a quantum without chemical altera-

tion may subsequently meet a second molecule, with the result that the change $2NH_3 = N_2 + 3H_2$ occurs, for which q possesses a smaller value than for the decomposition of a single molecule into its constituent atoms. Processes in which the production of a false equilibrium is accompanied by a decrease and an increase of the free energy of the system are described respectively as photochemical actions of the first and second class. The photochemical yield is the proportion of the absorbed radiation which undergoes conversion into chemical energy, and in the case of the decomposition of ammonia by the wave-length 0·209 amounts to 2%, a notable parallelism appearing to exist between the yields and those of the silent discharge. If the quantum is greater than the heat change in the primary photochemical process, the excess will be converted into heat, and heat will also be produced in the secondary processes. If in a photolytic process the highest possible photochemical yield is desired and a minimum heat effect, it is necessary that the quantum should be greater than the heat change involved in the primary process, but only greater to the extent required for the fission of the photolyte, and the heat effect in the secondary processes should be as small as possible.   D. F. T.

True Photochemical Processes. FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1917, **23**, 357—368).—A theoretical paper in which, after differentiating between ideal and real photochemical processes, and surveying a number of real photochemical reactions, the author propounds a theory of the mechanism of these processes. It is shown that a transformation of light energy into other forms of energy only occurs when the electrons rotating round the positive nucleus travel in a distorted path and when the distortion is produced by neighbouring particles which are in irregular relative motion. There must be, therefore, an optical coupling, in the sense of Stark's intermolecular influence, which is closely connected with the broadening of spectrum lines. According to the Le Chatelier-van't Hoff principle, it is to be expected that a change in the system will be brought about by the absorption of light, in the sense that the distortion will be as far as possible removed. This would occur most easily by the separation of the distorting particles from one another. The foregoing is in accord with Bohr's work (A., 1913, ii, 689, 943, 1045), and is sufficient to include all known real photochemical phenomena and the transformation of light into heat. The " equivalent law " of Einstein holds for ideal photochemical reactions, and in its deduction simple processes, without the mutual influences of neighbouring particles, alone were considered. This law may be extended by the assumption that in real photochemical processes not a single molecule, but the whole of the optically coupled particles, take part in the absorption of an energy quantum, and that therefore changes must take place over the whole of this region. This region contains fewer particles the higher the frequency of the absorbed light and the more dilute the partition of the mass; the lower the temperature, the more nearly the relationships approach those of an ideal

process. The more particles displaced by the absorption of an energy quantum, the larger is the fraction of the thermal energy lost. Hence in solid and stabilised systems, changes, brought about by the absorption of energy, persist for long periods and are the cause of characteristic changes and after-effects. Changes brought about in other bands by the distortion indicate the cause of a number of characteristic colour changes effected by light. This theory differs from previous theories, inasmuch as it does not presuppose either a primary electron emission or an electron loosening. The consideration of the fact that a relative displacement of small masses brings about a distortion of the electron orbit leads at once to the meaning of luminescence phenomena. Should the displacement be the result of light absorption, then fluorescence follows. In connexion with the foregoing, the author briefly considers the photoelectric effect and the action of Röntgen rays. It is shown, in the first place, that a connexion between photochemical fluorescence and photoelectric effects does not of necessity exist, but they can in individual cases appear simultaneously. The only direct process necessarily connected with the absorption of light is the relative displacement of the individual optically coupled particles, and therewith a change in the absorption under consideration, which shows itself most clearly by its dependence on the intensity of the incident rays.   J. F. S.

The Disintegration Constant of Radiothorium. B. Walter (*Physikal. Zeitsch.*, 1917, **18**, 584—585).—Measurements on the decay of the radiation, through 5 mm. of lead, of two preparations of radiothorium, extending over 500 days, have given a mean value for the half-period of 1·876 years, or 685 days, or 989 days for the period of average life. This is less than the accepted half-period, 2 years, and is in agreement with the recent statement of Meyer and Paneth (*Wien. Ber.*, 1916, Abt. II.*a*, **125**, 1253) that the value could not be greater than 1·9 years as a maximum.   F. S.

"Spark-lengths" in Hydrocarbon Gases and Vapours. Robert Wright (T., 1918, **113**, 79—80. Compare A., 1917, ii, 403).—Comparative measurements of the spark-lengths have been made in hydrogen, benzene, toluene, and paraffin hydrocarbons. In the paraffin series, the spark-length decreases with increase in the molecular weight of the hydrocarbon. The insulating power of *iso*pentane is exceptionally high, being greater than that of *n*-pentane and greater also than that of hexane. The results for benzene and toluene show that the insulating power of these is approximately the same as that of hexane.   H. M. D.

The Charge and Dimensions of Ions and Dispersoids. G. von Hevesy (*Kolloid Zeitsch.*, 1917, **21**, 129—136. Compare A., 1916, ii, 594).—Evidence is put forward in support of the view that there is a tendency for electrically charged particles to

combine with water molecules until the potential of the particle is reduced to about 70 millivolts. Since the potential of a charged ion is given by $V = \epsilon/KR$, where ϵ is the charge, R the radius of the particle, and K the dielectric constant of the solvent medium, it follows that $R = 2\cdot8 \times 10^{-8}$ cm. for a normal univalent ion. For a multivalent ion, the radius will be proportional to the charge.

Since the rate of diffusion of an ion depends mainly on the radius, the diffusion constants may be expected to depend on the valency. The available data for uni-, bi-, ter-, and quadri-valent ions give average values for the reciprocals of the diffusion constants, which are in the ratio $1:1\cdot99:3\cdot03:3\cdot88$. This relation is considered to afford strong support for the theory of constant ionic potential.

The combination which takes place when multivalent electrolytes are dissolved in water is supposed to be directly connected with the formation of aqueous envelopes in accordance with the above tendency. This combination is relatively small in the case of univalent electrolytes.

The ionic mobility of a normal univalent ion, for which $\epsilon = 4\cdot7 \times 10^{-10}$, $R = 2\cdot8 \times 10^{-8}$ cm., and $V = 0\cdot07$ volt, is 48 when expressed in terms of the ordinary units. In the case of ions of large size, such as complex organic ions, there is no tendency to combine with water, in that the potential of the anhydrous ion is already less than that which tends to be set up by the interaction. In a certain sense, these slowly moving ions are to be regarded as abnormal.

The same tendency is supposed to operate in the case of colloidal particles. On the assumption that these particles are characterised by an electrical double layer at the surface of contact with the dispersive medium, the potential of the particles may be calculated from the equation $V = \epsilon(R_2 - R_1)/KR_1R_2$, in which R_1 is the radius of the colloidal particle and $R_2 - R_1$ the thickness of the electrical double layer. This thickness has been found to be about 5×10^{-7} cm.

Since the mobility of the colloidal particles is of the same order as the normal ionic mobility, it is possible to utilise the above relation to obtain the connexion between the charge on a colloidal particle and its radius. It is thus found that the charge is approximately proportional to the radius in the case of very small particles, but that the charge increases much more rapidly than the radius.

In concentrated solutions of electrolytes, the ions are not entirely independent, and by taking into account the electrical interaction, it is inferred that the mobility of ions in aqueous solutions will increase with the concentration of the ions provided that a suitable correction is introduced for the change in viscosity.

In the case of fused salts, the mutual interaction becomes much more pronounced, and at the same time the proportion of neutral molecules with which the ions may combine is greatly reduced, with the result that the normal potential cannot be set up. The elec-

trical properties of fused electrolytes, and in particular the high electrical conductivity, are to be explained in terms of these peculiarities, which distinguish the fused salts from ordinary solutions of electrolytes.   H. M. D.

The Conductivity of Dispersoids. G. von HEVESY (*Kolloid Zeitsch.*, 1917, **21**, 136—138. Compare preceding abstract).—If the number, size, and mobility of the particles of a colloid are known, it is possible to calculate the charge on the particles and also the conductivity of the colloidal solution.

By calculating the conductivity of a 0·1% solution of colloidal gold on various assumptions relative to the radius of the particles and comparing the results with the observed conductivity, it is possible to derive information with respect to the actual size of the particles and the charge which they carry. It is probable that the maximum conducting power of a solution of a colloidal metal is less than $0·5 \times 10^{-5}$ mho, and the size of the particles which correspond with this is represented by $R = 10^{-7}$ cm., where R is the radius.

Although other colloidal substances appear to conduct somewhat better than the colloidal metals, the conductivity would appear to be in all cases less than that of a $0·0001N$-salt solution. The small conducting power of the colloids is to be attributed entirely to the small number of the particles, for the charge carried by the particles is always greater than the charge of an ion of the same size. The ratio of the charges is, in fact, given by $(R/d + 1)$, where R is the radius of the particle and d the thickness of the electrical double layer $= 5 \times 10^{-7}$ cm.   H. M. D.

Fallacy of Determining the Electric Charge of Colloids by Capillarity. A. W. THOMAS and I. D. GARARD (*J. Amer. Chem. Soc.*, 1918, **40**, 101—106).—It has been suggested that positive and negative colloids can be distinguished by the difference in the capillary effects which are observed when strips of filter paper are dipped into the colloidal solutions. If the particles are negatively charged, they are said to ascend the strip readily, whereas positively charged particles are coagulated and deposited on the filter paper within a short distance of the surface of the solution.

Experiments made with colloidal solutions of ferric hydroxide, chromium hydroxide, arsenious sulphide, antimony sulphide, and molybdenum lead to the conclusion that the basis of the above method is illusory, and that there is no relation between the sign of the electrical charge and the capillary behaviour. The ascent of the colloidal particles depends on the dilution of the sol, on the presence of electrolytes, on the nature of the surrounding atmosphere, and on the nature and previous treatment of the filter-paper strip. It is probable that the supposed dependence of the capillary behaviour on the charge of the particles owes its origin to the circumstance that the observations were made with relatively concentrated solutions of the positive colloids, the negative colloidal solutions being relatively dilute.   H. M. D.

Electrochemical Behaviour of Nickel. A. SMITS and C. A. LOBRY DE BRUYN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 394—403).—Certain anomalies exhibited by nickel in its electrochemical behaviour are attributable to the slow rate at which internal equilibrium is established. In contact with air or hydrogen, the anomalous behaviour is intensified, and this appears to be due to the circumstance that oxygen and hydrogen exert a negative catalytic influence. This influence of hydrogen explains the fact that the potential of a nickel electrode in contact with an atmosphere of hydrogen is the same as that of the hydrogen electrode. In reference to the normal calomel electrode, this potential is -0.640 volt, whereas the true equilibrium potential measured in a vacuum is -0.480 volt. To obtain this value, the hydrogen-ion concentration should not exceed 10^{-3} gram ion per litre.

H. M. D.

A Lead Standard Cell and a Determination of the Potential of the Lead Electrode. W. E. HENDERSON and GEBHARD STEGEMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 84—89).—It has been found that lead amalgams containing 2·5 to 6% of lead may be used for the attainment of constant and reproducible potential differences. The cell Pb amalgam | $PbSO_4$ | $Na_2SO_4,10H_2O$ | Hg_2SO_4 | Hg has an *E.M.F.* which may be represented by the equation $E_t = 0.96463 + 0.000174(t-25) + 0.00000038(t-25)^2$ for temperatures between 18° and 30°. The *E.M.F.* is reproducible to within three-hundredths of a millivolt, but a gradual diminution of the *E.M.F.* occurs when the cell is kept for an extended period of time.

From the temperature coefficient of the cell, the heat of the reaction, $0.5Pb_2Hg + Hg_2SO_4 = PbSO_4 + 2.5Hg$, is found to be 42139 cal. The value derived from thermochemical data is 41785 cal.

Measurements of the *E.M.F.* of a cell of the above type with the amalgam replaced by pure lead gave 0·96973 at 25°. The difference of 0·0051 volt is used in the derivation of the *E.M.F.* of the cell Pb | $PbCl_2$ | $0.1NKCl$ | Hg_2Cl_2 | Hg, giving 0·5187 volt at 25°. This is further employed in the calculation of the potential of the normal lead electrode, using available data for the solubility and degree of ionisation of lead chloride. The *E.M.F.* of the cell obtained by combination of the normal lead electrode with the $0.1N$-calomel electrode at 25° is 0·4696 volt. [See *J. Soc. Chem. Ind.*, 1918, March.] H. M. D.

Effect of Interionic Forces on Electrolytes. S. R. MILNER (*Phil. Mag.*, 1918, [vi], **35**, 214—220).—The author contends that the true degree of ionisation of an electrolyte cannot be obtained from either osmotic or conductivity data. The failure of the law of mass action in its application to solutions of strong electrolytes is said to be such that insuperable difficulties stand in the way of any theory which ascribes the variations in conductivity to changes in the number of the ions. These difficulties are avoided if the

variations in conductivity are attributed to the action of the electrical field on the ionic mobility. H. M. D.

Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. I. The Water Correction. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 106—122).—The introduction of improvements in the Kohlrausch method for the determination of the conductivity of electrolytes (compare A., 1917, ii, 10) has made it possible to obtain increased accuracy in the experimental measurement, and to investigate, in particular, the conductance of electrolytes in very dilute solution. In this paper, which forms the first of a series in which the results of these investigations are described, the author discusses the question of the magnitude and nature of the water correction, the influence of carbonic acid, and the products to which this gives rise by metathesis in dilute solutions of various kinds of electrolytes. The fact that the strong acids in very dilute solution appear to be abnormal in their conducting power, even when the observed conductivity has been corrected for carbonic acid, suggests strongly that basic or saline impurities are present, and since these affect the magnitude of the carbonic acid correction, it is considered that accurate data for the conductivity of dilute solutions can only be obtained by the use of ultra-pure water instead of water which is in equilibrium with the atmosphere. H. M. D.

Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. II. The Extrapolation of Conductivity Data to Zero Concentration. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 122—131).—The methods previously employed by Kohlrausch, Noyes, Kraus and Bray, and by Bates for the estimation of the limiting molecular conductivity are critically examined and rejected as untrustworthy on the ground that most of these involve the assumption that the functional relation between the conductivity and the concentration, which holds for the lowest measurable range of concentrations, will also hold down to zero concentration.

A new graphical method of extrapolation is described, by which the author claims to avoid the errors involved in the "arbitrary function" methods and also those which attach to direct graphical extrapolation. The proposed method rests on two assumptions, the first of which is that with decreasing concentration (c), the value of $ca^2/(1-a)=k$ decreases and approximates to a constant value k_0 at extreme dilutions. According to the second assumption, the relation between c and k must be such that deviations from the law of mass action do not increase with the dilution. The actual procedure in applying the method consists in plotting values of k against values of c for different assumed values of Λ_0, and rejecting those values which cause the curve to exhibit radical changes in direction in the region of very dilute solution. It is said to be possible to determine Λ_0 with a precision of 0.01% if the conductivity data are of this order of accuracy and extend to $c = 0.00002$.

The method of extrapolation described by Bates (A., 1913, ii, 466) involves the assumption of the validity of the Storch equation, but otherwise resembles the method now proposed, and when applied to the data for potassium chloride gives very nearly the same result.   H. M. D.

Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. III. A Study of Dilute Solutions of Potassium Chloride. HENRY J. WEILAND (*J. Amer. Chem. Soc.*, 1918, **40**, 131—150).—A method for the preparation of "ultra-pure conductivity water" is described in which ordinary conductivity water ($k = 0.6$ to 0.8×10^6 mho) is heated to near its boiling point in a large quartz still, a current of carefully purified air being passed through the water. The water vapour is condensed in a block-tin tube and collected in a quartz receiver. The specific conductance of the water obtained in this way may vary from 0.05 to 0.07×10^{-6} mho at 18°, and has been used in the investigation of the conductivity of very dilute solutions of potassium chloride.

The conductivity cell, of about 3 litres capacity, is made of quartz, and is provided with co-axial cylindrical platinum electrodes, which are so constructed that the water does not come into contact with anything but platinum or quartz. The dilute solutions examined were prepared in the cell out of contact with the atmosphere by the successive introduction of small crystals of potassium chloride weighing about 0.005 gram.

The error resulting from the adsorption of salt from these dilute solutions by the quartz surface of the cell has been examined and found to be negligible.

The experimental data for solutions varying in concentration from about $0.00001N$ to $0.001N$ show that the quantity $k = c\alpha^2/1 - \alpha$ has a constant value for solutions for which the concentration is less than $0.0001N$. The results afford, therefore, direct experimental proof of the validity of the mass law in its application to the ionisation of potassium chloride at very low concentrations. The limiting value of the equivalent conductance at 18° was found to be 129.64 ± 0.02 (compare preceding abstract).

The empirical relations suggested by Bates and by Kraus for use in extrapolating to zero concentration have been tested by reference to the data for solutions between $c = 0$ and $c = 0.005$, and the conclusion is drawn that these do not reproduce satisfactorily the experimental results over this range of concentrations.
                                                    H. M. D.

Equivalent Conductance of Electrolytes in Dilute Aqueous Solution. IV. Two Laws Governing the Ionisation Equilibrium of Strong Electrolytes in Dilute Solutions, and a New Rule by means of which the Equivalent Conductance at Infinite Dilution can be Determined from a Single Conductance Measurement. EDWARD W. WASHBURN (*J. Amer. Chem. Soc.*, 1918, **40**, 150—158).—The behaviour of

electrolytes in very dilute solution, as exemplified by the data for potassium chloride in the preceding paper and by the most accurate conductivity work of Kohlrausch and his collaborators, has led the author to the following general conclusions. In sufficiently dilute solutions ($c < 0.0001N$), all uni-univalent salts of strong acids and bases are ionised in accordance with the requirements of the law of mass action, and the ionisation constant is the same for all. The values of $k = ca^2/1-a$ for such salts are identical in sufficiently dilute solution, and this identity persists up to concentrations which are higher the more closely the salts under comparison resemble each other. According to this second generalisation, the identity in the ionisation relations extends beyond the concentration up to which the salts in question satisfy the requirements of the mass law. In terms of the equation $\Lambda_c{}^2C/\Lambda_0(\Lambda_0 - \Lambda_c) = K$, the statement implies that K is independent of the nature of the salt, and on simplification this equation leads to the relation $\Lambda_0 = \Lambda_c/a$, where a is independent of the nature of the salt. For $C = 0.0001N$ this equation becomes $\Lambda_0 = 1.00475 \Lambda_c$.

Evidence in support of the above conclusions is furnished by the data for the salts of the alkali metals, which are examined in detail. H. M. D.

Electrolytic Deposition of Alloys and their Metallographic and Mechanical Investigation. VIII. Cathodic Deposits of Iron and Iron–Nickel Alloys obtained at the Ordinary Temperature under High Hydrogen Pressure. ROBERT KREMANN and HERMANN BREYMESSER (*Monatsh.*, 1917, **38**, 359—384. Compare A., 1915, ii, 511).—In previous papers (*loc. cit.*) it has been shown that electrolytic iron deposited at ordinary pressures and temperatures is charged with hydrogen and admixed with ferric hydroxide; it is also brittle and hard. These conditions are shown to be due to the simultaneous liberation of hydrogen at the cathode. It is shown theoretically that the simultaneous liberation of hydrogen can be prevented if the electrolysis is carried out under a high hydrogen pressure. To test this deduction, N-solutions of ferrous sulphate have been electrolysed under a pressure of 20 atm. of hydrogen with a *C.D.* of 0.25 amp./dm^2 and 0.75 amp./dm^2. A further series of experiments was carried out with solutions to which 10 grams of citric acid per litre were added. In the first two cases, it is shown that the current efficiency is 99.33—99.46%, whereas in the last case it is only 88.57%. The deposits obtained in these cases have been compared with those obtained under 1 atm. pressure of hydrogen and in the presence of 0.15N-sulphuric acid. It is shown that the material obtained under the higher pressure is composed of larger crystals than that under the lower pressure. The hydrogen content of the high-pressure specimens is much less than that of the low-pressure specimens, whilst the hardness is very much reduced by the deposition under high hydrogen pressure. The specimens obtained under the present conditions are much less brittle than those obtained under other conditions, whereas the magnetic properties of the deposits

are not affected by change in the conditions of deposition. Electro
lytic iron produced under pressure when immersed in N-ferrous
sulphate solution shows at once the equilibrium potential of -0.417
volt, whilst iron deposited under other conditions only reaches this
value after some considerable time.

A further series of experiments was made under similar condi-
tions with mixed solutions of ferrous sulphate $0.7N$ and nickel
sulphate $0.3N$. In this case, the nickel–iron deposits did not show
the improvement observed in the case of iron alone. A number
of microphotographs of the deposits is appended to the paper.
[See also *J. Soc. Chem. Ind.*, 1918, March.]   J. F. S.

Temperature Determinations by Eutectic Alloys. CHARLES
P. STEINMETZ (*J. Amer. Chem. Soc.*, 1918, **40**, 96—100).—
Eutectic points of alloys furnish a more satisfactory means for the
determination of temperature than the melting points of pure
metals. In general, the eutectic point is not dependent to the
same extent on the purity of the substance, and the alloys afford
a more numerous series of fixed points on the scale.

The cooling curves of a number of alloys have been examined,
and twelve of these found to give satisfactory eutectic tempera-
tures ranging from $69.5°$ to $194.0°$. The approximate composition
of these low-melting eutectic alloys is recorded in the paper. [See
J. Soc. Chem. Ind., 1918, March.]   H. M. D.

**Solubility of Sodium Sulphate as a means of Determining
Temperatures.** THEODORE W. RICHARDS and VICTOR YNGVE (*J.
Amer. Chem. Soc.*, 1918, **40**, 164—174).—The solubility of a sub-
stance with a large temperature coefficient may be used for the
accurate measurement of temperatures. Between $15°$ and $25°$, the
solubility of sodium sulphate varies rapidly with the temperature,
and since it may easily be obtained in a pure condition and readily
gives a saturated solution, it has been examined with a view to its
application in the measurement of temperature.

Measurements of the solubility were made at accurately deter-
mined temperatures in the neighbourhood of $15°$, $17.5°$, $20°$, and
$25°$. The results are represented very closely by the equation
$\log s = 0.659970 + 0.02963889t + 0.0000688925t^2$, in which s is the
solubility expressed as the number of grams of sodium sulphate
per 100 grams of water.

It is claimed that the solubility method described will permit
of the determination of temperatures to within $0.01°$, and may be
used for the standardisation of thermometers.   H. M. D.

**The Transition Temperatures of Strontium Chloride and
Strontium Bromide as Fixed Points in Thermometry.**
THEODORE W. RICHARDS and VICTOR YNGVE (*J. Amer. Chem.
Soc.*, 1918, **40**, 89—95).—The transition temperatures have been
determined by methods described in previous papers (compare A.,
1914, ii, 244).

The purification of strontium chloride can be effected by re-

crystallising above and afterwards below the transition temperature. It is found that barium can be readily removed by recrystallising below the transition temperature (61°), so as to obtain the hexahydrate. The calcium cannot be removed in this way, but recrystallisation above the transition temperature yields the dihydrate, from which the calcium is rapidly eliminated.

In a similar way, strontium nitrate may be purified by crystallising out under conditions which yield the anhydrous salt, whereby the calcium is removed. The barium may then be removed subsequently by recrystallising the hexahydrated chloride prepared from the partially purified nitrate.

The temperature at which the hexahydrate of strontium chloride is transformed into the dihydrate has been found to be 61·341° at atmospheric pressure on the hydrogen scale.

Preliminary experiments show that hexahydrated strontium bromide is similarly transformed into the dihydrate at about 88·62°. [See *J. Soc. Chem. Ind.*, 1918, 109A.]   H. M. D.

Theory of Specific Heats. WALTHER JANKOWSKY (*Zeitsch. Elektrochem.*, 1917, **23**, 368—371).—A theoretical paper in which, on the basis of the older kinetic theory, it is shown that without making an assumption of an equal partition of energy it is possible to derive a formula for the specific heat of gases and vapours. This formula has the form $c = e_m n(1 + i)/m \cdot n \cdot i$, in which c is the true specific heat, that is, the heat at constant volume, e_m the mean energy change, expressed in calories, of a molecule when the temperature is raised 1°, i is the ratio of the change of molecular energy to that of the sum of the atomic energies, $i = e_m / e_a \cdot n$, and n is the number of atoms in the molecule. This formula is tested on a large number of gases and vapours, and is found to give good agreement. The dependence of the specific heat on temperature is shown to be due to changes in the value of i. This is a direct contradiction of the theory of equal energy partition. This formula gives a simple theoretical basis to the Law of Dulong-Petit and Joule, and explains quantitatively the divergencies, and also shows that a strict following of the law is impossible. A further formula is deduced for the calculation of the ratio of the specific heat at constant pressure to that at constant volume. This has the forms $k = 1 + 2C/3c_v m$ and $k = 1/1 - 2C/3c_p m$, in which $C = 2·98$, $k = c_p/c_v$, and m is the molecular weight.   J. F. S.

Calculation of Gas Equilibria. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 270—272).—A mathematical paper, in which by a series of approximations the author shows that the value of a, the chemical constant, which is expressed by Planck as $a = R \log_e p - C'p \log_e T + r_0/T$, can on thermodynamic grounds be proved to have the value $a = R \log_e p + r_0/T - Cp \log_e T$. In both equations p is the vapour pressure, $C'p$ the specific heat at constant pressure of the vapour, r_0 the heat of vaporisation at absolute zero, and Cp the specific heat of the liquid phase.   J. F. S.

Specific Heat of Liquid Ammonia. NATHAN S. OSBORNE and MILTON S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1918, **40**, 1—13).—Measurements of the specific heat of liquid ammonia have been made according to two independent methods. In one of these, the change in temperature produced by a measured quantity of heat under saturation conditions was determined, whilst in the other the calorimeter was kept full of liquid at constant pressure greater than the saturation pressure, the change in temperature produced by the added heat energy being corrected for the heat content of the expelled liquid.

The interval of temperature covered by the measurements ranges from $-45°$ to $45°$, and over this range the specific heat increases from $1·058$ at $-45°$ to $1·173$ at $45°$. The dependence of the specific heat on the temperature is represented by the empirical equation $c = 0·7498 - 0·000136\theta + 4·0263 / \sqrt{133 - \theta}$, in which c is expressed in terms of the $20°$ calorie and θ is the temperature. H. M. D.

Latent Heat of Vaporisation of Ammonia. NATHAN S. OSBORNE and MILTON S. VAN DUSEN (*J. Amer. Chem. Soc.*, 1918, **40**, 14—25).—The calorimeter used in the determination of the specific heat of liquid ammonia (compare preceding abstract) was modified so as to render it suitable for the measurement of the heat of vaporisation. A known quantity of heat, developed and measured electrically, is employed to vaporise a portion of the liquid ammonia contained in the calorimeter, the ammonia vapour being withdrawn at measured temperature and pressure and its amount estimated. Corrections due to thermal leakage were reduced to a minimum by special methods of manipulation.

The results obtained show that the latent heat of vaporisation decreases from $333·0$ cal. at $-42°$ to $252·6$ cal. at $49°$. The variation of the latent heat with the temperature may be expressed by the empirical equation $L = 32·968 \sqrt{133 - \theta} - 0·5895(133 - \theta)$, in which θ represents the actual temperature and 133 represents the critical temperature.

From the latent heat of vaporisation and the specific heat of the liquid under the pressure of its saturated vapour, the authors have calculated the specific heat of saturated ammonia vapour. Expressed in joules per gram per degree, this varies in a continuous manner from $-4·42$ at $-45°$ to $-3·36$ at $45°$. To reduce these numbers to $20°$ calories, they must be divided by $4·163$. H. M. D.

The Vapour Pressure of Liquid Ammonia up to the Critical Temperature. II. FREDERICK G. KEYES and R. B. BROWNLEE (*J. Amer. Chem. Soc.*, 1918, **40**, 25—45).—The vapour pressures of liquid ammonia have been measured between $0°$ and the critical temperature by a method involving the use of a piston gauge. The dependence of the vapour pressure on the temperature may be expressed by the equation $\log p = -1969·65/T + 16·19785 - 0·0423858T + 5·4131 \times 10^{-5}T^2 - 3·2715 \times 10^{-8}T^3$. This

equation holds satisfactorily for vapour pressures down to the freezing point ($-77°$). The boiling point was found to be $-33\cdot20\pm0\cdot05°$.   H. M. D.

Formula giving the Saturated Vapour Pressure of a Monatomic Liquid. E. Ariès (*Compt. rend.*, 1918, **166**, 193—197). —The author deduces the formulæ $\Pi = \tau^{\frac{5}{2}}Z/x$ and

$$x = \left(1 + \frac{(1-\tau)(0\cdot84 - \tau)}{2\tau^2 + 1\cdot20}\right)\tau^{\frac{3}{2}},$$

where τ is the reduced temperature and Π is the reduced pressure of the saturated vapour, and shows that the calculated results agree with the observed results in the cases of krypton, xenon, and argon.   W. G.

Vapour Pressures of Liquid Metals. Joel H. Hildebrand (*J. Amer. Chem. Soc.*, 1918, **40**, 45—49).—It has been shown previously (A., 1915, ii, 416) that the heat of vaporisation divided by the absolute vaporisation temperature is the same for all normal liquids provided that comparison is made at temperatures for which the concentrations of the saturated vapours have the same value. On the basis of this relation, it is possible to superimpose the vapour-pressure curve for one substance on that of another by means of a single constant, a, which expresses the ratio of the absolute temperatures referred to above.

By taking mercury as the standard liquid, for which the vapour pressure may be represented by the equation $\log p = -3140/T + 7\cdot85$, it is shown that the vapour pressures of a number of other liquid metals may be expressed by the equation $\log p = -3140a/T + 7\cdot85 + \log a$, in which a varies from $1\cdot74$ for cadmium to $4\cdot90$ for iron.

By means of the tabulated values of a for the different metals, it is possible to calculate the vapour pressure at any temperature and also the heat of vaporisation.   H. M. D.

Apparatus for the Determination of Boiling Points. Alfred Edwards (*J. Soc. Chem. Ind.*, 1918, **37**, 38t).—A simple form of boiling-point apparatus is described which provides for the complete immersion of the thermometer stem in the heated vapour. The still-head is traversed by a somewhat narrower inner tube with a hole near the top, through which the vapour from the boiling liquid escapes into the outer tube, passing therefrom to a condenser tube which is sealed into the still-head at its lower end. The condensed liquid tends to seal the space between the inner and outer tubes in its lower portion, and thereby to secure a regular stream of vapour through the inner tube in which the thermometer is supported.   H. M. D.

The Heat of Formation of Liquid Water from its Ions. J. A. Muller (*Bull. Soc. chim.*, 1918, [iv], **23**, 8—13).—Using the method previously described (compare A., 1913, ii, 115), the

author has determined the heats of reaction of sulphuric and hydrochloric acids with potassium hydroxide in aqueous solution at infinite dilution, and from his results has calculated the heat of formation of water from its ions. The values obtained were, with sulphuric acid 13,966 cal., and with hydrochloric acid 14,003 cal.   W. G.

Thermochemical Studies. The Heat of Combustion of the Paraffins. DANIEL LAGERLÖF (*J. pr. Chem.*, 1917, [ii], **96**, 123—124. Compare A., 1905, ii, 76).—The heat of combustion of *n*-octane observed by direct measurement (Richards and Jesse, A., 1910, ii, 269) agrees closely with the value calculated with the aid of the author's hypothesis (*loc. cit.*), which thereby receives confirmation.   D. F. T.

The Heat of Ionisation, in Aqueous Solution, of Crystalline Barium Sulphate and the Solubility of this Salt in Water. J. A. MULLER (*Bull. Soc. chim.*, 1918, [iv], **23**, 13—16).—From measurements of the heats of reaction of barium chloride and sulphuric acid at increasing dilutions, and determining the limits towards which these tend at three temperatures, the following expression is found for the value of q, the heat of combination of the ions Ba and SO_4, $q = 105502\cdot32 - 696\cdot857T + 1\cdot2118T^2$, T being the absolute temperature. The heat of ionisation of crystalline barium sulphate in aqueous solution is the inverse of this. From this it is possible to calculate the ratio of the solubilities of barium sulphate at different temperatures, and the results agree with those of van't Hoff. [See also *J. Soc. Chem. Ind.*, 1918, March.]
                                                                    W. G.

Adsorption Compounds and Adsorption. II. Replacement from the Surface. L. BERCZELLER and ST. HETÉNYI (*Biochem. Zeitsch.*, 1917, **84**, 118—136).—Stalagmometric measurements of the effect of addition of alcohols to solutions of various crystalloid and colloid substances.   S. B. S.

Utilisation of the Adsorptive Power of Fuller's Earth for Chemical Separations. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1918, **40**, 312—328).—A comparison has been made of the adsorptive capacities of thirty-six samples of fuller's earth and other similar clays by experiments on the adsorption of quinine bisulphate and methylene-blue. The adsorptive power of a given quantity of a particular sample increases with the concentration of the unadsorbed substance in the aqueous solution and also with the time of contact, although the rate of adsorption gradually diminishes.

The method of measurement consisted in mixing 1 gram of the fuller's earth sample with 10 c.c. of water and adding to the mixture measured volumes of 1% quinine bisulphate or 0·5% methylene-blue solution. The tubes containing the mixtures were shaken for half an hour, and the solutions then examined for the adsorbed

substances. From a series of such tests it was possible to obtain comparative numbers for the adsorption powers of the samples.

In the case of both the quinine salt and the methylene-blue, the free base only is adsorbed. When both are present in the solution in equal amounts, they are adsorbed to very nearly the same extent. If the fuller's earth is first shaken with methylene-blue and then with quinine bisulphate, a small amount of the latter is adsorbed and only a trace of the former liberated. If the order is reversed, a much larger proportion of methylene-blue is adsorbed and a considerable amount of the quinine salt is displaced.

The experiments show, further, the influence of dilution, of the acidity of the solution, and of the presence of ethyl alcohol and sucrose. [See also *J. Soc. Chem. Ind.*, 1918, March.]

H. M. D.

Preparation of Uniform Collodion Membranes for Dialysis. CHESTER J. FARMER (*J. Biol. Chem.*, 1917, **32**, 447—453. Compare Brown, A., 1917, ii, 362).—The membrane is prepared by filling a glass tube with collodion solution, inverting, and allowing to drain for one minute. The tube is then dried in a current of air for one minute and afterwards filled with cold water. After a few minutes, the thin membrane can be removed from the walls of the glass tube with the aid of a pair of forceps. Convenient apparatus for performing these operations is described in detail in the original paper. H. W. B.

The Colloidal Membrane : its Properties and its Function in the Osmotic System. FRANK TINKER (*Trans. Faraday Soc.*, 1917, **37**, 133—140).—Although it is probable that the average kinetic energy of a molecule in the liquid state is the same as in the state of vapour, this must not be taken to imply that the average pressure of a solute molecule has the same value in the two states. In the solution, a large proportion of the volume is occupied by the solvent molecules, with the result that the free space is greatly reduced, and the pressure which the solute molecules would exert on an imaginary flame is consequently much greater than the corresponding gas pressure.

The internal bombardment pressure of the solute must therefore not be confused with the osmotic pressure, which, in the author's opinion, is an external mechanical pressure. The supposed analogy between osmotic and gas pressure is also considered to have no real foundation, in that this analogy fails to account for the fundamental phenomena of diffusion. The mechanism involved in an osmotic system is said to be quite different from that which produces gas pressure, there being no pressure on the membrane unless the solution is compressed. This pressure is then exerted by the solution as a whole and not by the individual molecules, whether of solute or solvent.

The similarity between a dilute solution and a gas is due to the fact that both experience no change in internal energy when the

volume is varied. Equality in this respect does not, however, afford any proof that the mechanism involved in gas and osmotic pressure is of the same nature.

Reference is made to the importance of the study of the properties of the membrane, and a brief account is given of the author's work on this subject.   H. M. D.

Kinetic Theory of Osmotic Pressure. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1917, **13**, 123—132).—The cause of osmotic pressure is discussed, and it is pointed out that the kinetic theory is the only theory yet advanced which reproduces directly the values for the osmotic pressure which have been actually obtained in experiments with dilute solutions. The arguments against the kinetic theory, which rest largely on the dissimilarity of the conditions in liquids and gases, have been greatly weakened as the result of observations on the Brownian motion. These observations afford the experimental basis for a kinetic theory of liquids, according to which solute and solvent molecules are in a state of rapid movement. The osmotic pressure represents the dynamical effect of this thermal motion of the solute molecules, and in order to obtain a mental picture of the effect of the presence of the solute, it may be supposed that the molecular bombardment of the molecules of the solute on the boundary surface tends to enlarge the boundaries, and thereby to relieve the total pressure on the solvent. In other words, the kinetic pressure resulting from the thermal agitation of the solute molecules acts outwardly and diminishes the Laplacian pressure by an equivalent amount.

It is shown that the data for the osmotic pressures of sucrose solutions at 20° can be represented satisfactorily by the equation $P(v - b) = RT$, in which b is a constant which is greater than the volume of the sucrose. On the assumption that this is due to the hydration of the sucrose molecules, it is found that about 5·3 molecules of water are associated with a molecule of sucrose.

If this equation is applied to the whole of Morse's results and hydration values calculated for different concentrations and temperatures, the numbers are not quite regular, but show clearly that hydration diminishes with increasing concentration. The values for dilute solutions are surprisingly high, but are considered to be quite plausible, and it is suggested that the variation in solubility with the temperature may be due to changes in the degree of hydration.

According to the equation connecting osmotic pressure with the latent heat of dilution of the solution, the latter quantity depends on the variation of P/T with the temperature T. If these variations, derived from Morse's values at 10° and 30°, are compared with those calculated from measurements of the heat of dilution at 20°, the degree of correspondence is found to be quite satisfactory.   H. M. D.

Osmotic Pressure in Relation to the Constitution of Water and the Hydration of the Solute. W. R. BOUSFIELD (*Trans. Faraday Soc.*, 1917, **13**, 141—155).—The author's previous

work on the properties of solutions is considered with reference to the kinetic interpretation of osmotic pressure. This interpretation rejects the idea that the molecules of the solute are directly responsible for the osmotic pressure, and a modified gas theory is put forward which involves the assumption that water is a mixture of three kinds of molecules, vapour, liquid, and ice molecules, represented by H_2O, $(H_2O)_2$, and $(H_2O)_3$ respectively, and attributes the osmotic pressure to the thermal agitation of the vapour molecules. The validity of the ideal gas equation for dilute solutions is supposed to indicate that these hydrol molecules comport themselves towards changes of pressure and temperature in the same way as the molecules of a gas.

The addition of a solute to water is said to be accompanied by a reduction in the proportion of both the vapour and ice molecules in the equilibrium mixture, resulting in a diminution of the vapour pressure and a lowering of the freezing point. Reduction of the molecular interspace by external pressure raises the vapour pressure, and the osmotic pressure is defined as the liquid pressure under which the external vapour pressure of a solution is equal to the internal vapour pressure of the pure solvent.

The relations between the osmotic pressure, the lowering of the vapour pressure, and the freezing point are discussed in reference to the above theory, and it is claimed that the various osmotic data are brought into line with other properties by the assumption that the active hydrol molecules enter into combination with the solute molecules. It is said that different properties lead to the same value for the degree of hydration of the solute.   H. M. D.

Solubility and Internal Pressure.   JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1918, **40**, 198).—Corrections to a previous paper (this vol., ii, 36).   H. M. D.

Changes in Volume during Solution.   III.   GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1918, **40**, 192—193).—If AB, $A'B'$, AB', and $A'B$ represent the four salts formed by the ions A, B, A', and B', then the apparent volume in solution of one of these may be obtained if the apparent volumes in solution of the three others are known. The calculation depends on the fact that the sum of the apparent volumes of AB and $A'B'$ is equal to the sum of the apparent volumes of AB' and $A'B$.

The apparent volume of dissolved calcium carbonate obtained in this way from the apparent volumes of calcium chloride, sodium carbonate, and sodium chloride is 3·0 c.c. Since the molecular volume of solid calcium carbonate is 36·9 c.c., the change in volume on dissolution is $3·0 - 36·9 = -33·9$ c.c. per mol. The contraction is thus more than 90% of the volume of the solid salt.   H. M. D.

The Structure in Steps in certain Anisotropic Liquids. F. GRANDJEAN (*Compt. rend.*, 1918, **166**, 165—167).—This structure, already found in ethyl azoxybenzoate and cinnamate (compare *Bull. Soc. franç. Min.*, **39**, 167), has been found also in the

oleates and the positive phase of cholesteryl decoate. It is described in detail. This structure in steps, and particularly the existence of steps of extremely slight thickness, separated from steps infinitely near by abrupt lateral surfaces, reveals a discontinuous property of the liquid, which is not observed in the group of azoxyphenetole.

W. G.

Precipitation of Colloidal Gold and Platinum on Metallic Surfaces. ELLWOOD B. SPEAR and KENNETH D. KAHN (*J. Amer. Chem. Soc.*, 1918, **40**, 181—184).—The precipitation of colloidal gold and platinum solutions when brought into contact with polished plates of zinc, steel, nickel, lead, tin, copper, or platinum has been examined, with results which indicate that the rate of coagulation increases with the electro-positive character of the metal. The effect also depends on the nature of the metal surface, in that the rate of coagulation for a given metal decreases if the surface is roughened or if the metal is employed in a finely divided condition.

It is suggested that ions of the active metal are formed, and that these are adsorbed by the colloidal particles, thereby neutralising their negative charge. In support of this view, it has been found that copper does not bring about coagulation if the colloidal gold or platinum solution is freed from air by the passage of a current of purified hydrogen. [See *J. Soc. Chem. Ind.*, 1918, March.]

H. M. D.

Laws of Chemical Equilibrium. ERSKINE D. WILLIAMSON and GEORGE W. MOREY (*J. Amer. Chem. Soc.*, 1918, **40**, 49—59). —A theoretical paper in which the authors derive general equations for the equilibrium in heterogeneous chemical systems by methods which are essentially based on the work of Gibbs. Special forms of equations applicable to systems of simple type are specifically referred to.

H. M. D.

Pressure–Temperature Curves in Univariant Systems. GEORGE W. MOREY and ERSKINE D. WILLIAMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 59—84. Compare preceding abstract).—The pressure-temperature curves for univariant systems are discussed in reference to Gibbs's equations. The conditions under which different pressure-temperature curves become coincident are examined, and a method is developed by which the order of succession of the pressure-temperature curves intersecting at an invariant point can be determined. The applicability of the method is shown by reference to the five curves which melt in the quintuple points characteristic of the ternary system H_2O–K_2SiO_3–SiO_2.

H. M. D.

Univariant Equilibria in the Ternary System–Water, Sodium Sulphate, Ammonium Sulphate. C. MATIGNON and F. MEYER (*Compt. rend.*, 1917, **165**, 787—789).—The experimental data recorded show the composition of solutions which are

in equilibrium with two solid substances. The two sulphates combine to form the double sulphate $NaNH_4SO_4,2H_2O$, and numbers are given for solutions saturated with respect to the double salt and Glauber's salt between $-13°$ and $25·5°$, double salt and anhydrous sodium sulphate between $29°$ and $58°$, double salt and ammonium sulphate between $-19°$ and $58°$, and with respect to anhydrous sodium sulphate and ammonium sulphate between $62·5°$ and $109°$.

A solution saturated with sodium sulphate boils at $102°$ and contains $2·10$ mols. per 1000 grams of solution. Similarly, the b. p. of saturated ammonium sulphate solution is $108·9°$, and it contains $3·922$ mols. per 1000 grams, whilst a solution saturated with respect to the two sulphates boils at $111°$ and contains $1·125$ mols. Na_2SO_4 and $3·175$ mols. $(NH_4)_2SO_4$ per 1000 grams of solution. [See, further, *J. Soc. Chem. Ind.*, 1918, 29A.]   H. M. D.

Heterogeneous Equilibria between Aqueous and Metallic Solutions. G. McP. SMITH and S. A. BRALEY (*J. Amer. Chem. Soc.*, 1918, **40**, 197).—A correction of results recorded in a previous paper (A., 1917, ii, 455).—The error necessitates a further investigation of the ionisation relations in mixtures of sodium and strontium chlorides.   H. M. D.

Invariant Equilibria in the Ternary System : Water-Sodium Sulphate–Ammonium Sulphate. C. MATIGNON and F. MEYER (*Compt. rend.*, 1918, **166**, 115—119).—A study of the equilibrium of the solution in the presence of the various combinations of three solid phases, the cooling curves being plotted. In a trilinear diagram, with co-ordinates giving respectively the temperature, the concentration of anhydrous sodium sulphate, and the concentration of ammonium sulphate, are shown the surfaces corresponding with the states of equilibrium of the solution with respect to one solid phase. [See also *J. Soc. Chem. Ind.*, 1918, March.]   W. G.

Effect of Hydrogen Chloride on the Nitrogen–Hydrogen Equilibrium. E. B. LUDLAM (*Trans. Faraday Soc.*, 1917, **13**, 43—52).—The observations made by Deville suggest that the stability of ammonia at high temperatures is increased very considerably by the presence of hydrogen chloride and lead to the supposition that the equilibrium between nitrogen, hydrogen, and ammonia will be displaced in favour of the ammonia if hydrogen chloride is added to the mixture.

Experiments in which a mixture containing equivalent quantities of nitrogen, hydrogen, and hydrogen chloride was subjected to the action of an electrically heated platinum wire or carbon rod stretched along the axis of a water-cooled tube afforded no evidence in support of the above hypothesis. The soaking of the carbon rod in solutions of sodium, calcium, or magnesium chloride made no difference to the result.

Other experiments, in which a mixture of nitrogen and hydrogen was passed slowly through a quartz tube containing sugar charcoal

at about 800° gave results which seemed to show that the ammonia formed was increased when hydrogen chloride was added to the nitrogen–hydrogen mixture, although the effect was much smaller than that calculated from the mass action equation.

On the assumption that the smallness of the effect was due to the slowness of the reaction, attempts were then made to approach the equilibrium condition by starting with ammonium chloride. Weighed quantities of this were accordingly heated in an evacuated quartz tube in presence of gold, silver, copper, and iron, with results which seemed to show that ammonium chloride is not nearly so stable at high temperatures as Deville's observations would suggest.

The evidence afforded by these experiments pointed to iron as the most active catalyst, and further observations were therefore made in which nitrogen, hydrogen, and hydrogen chloride were passed through a layer of iron asbestos heated at about 450°. Even at this low temperature, ferrous chloride is formed and sublimes, and the volatility of this substance would evidently be a serious obstacle to the use of iron in practice, even if the catalytic activity of the metal were very considerable.   H. M. D.

Equilibrium Data on the Polybromides and Polyiodides of Potassium. G. A. LINHART (*J. Amer. Chem. Soc.*, 1918, **40**, 158—163).—On the assumption that KBr_3 and KBr_5 are present in aqueous solutions which contain potassium bromide and bromine, the constitution of the solution is determined by the equations $[Br_3']/[Br'][Br_2] = K'$ and $[Br_5]/[Br_3][Br_2] = K''$. By reference to Worley's data for 26·5°, it is shown that K' remains very nearly constant = 15·9 if it is assumed that $K'' = 1·2$. At 0° $K' = 19·6$ and $K'' = 2·08$, and at 32·6° $K' = 15·5$ and $K'' = 1·06$.

From the values of the constants at the two lower temperatures, the author calculates the heat of the reactions $Br' + Br_2(aq) = Br_3' - 1290$ cal. and $Br_3' + Br_2(aq) = Br_5' - 3390$ cal.

When the value $K'' = 1·2$ for 26·5° is applied to solutions which are saturated with bromine, the calculated value of K' is appreciably higher than that indicated above, and it is suggested that this may be due to the formation of KBr_7.

Measurements of the ratio of distribution of iodine between carbon tetrachloride and water at 25° show that the ratio of the concentrations, expressed in mols. per 1000 grams of solvent, is constant = 57·7.

The constitution of iodine–potassium iodide solutions is also discussed briefly.   H. M. D.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. X. Equilibria in Binary Solutions of *p*-Toluidine and Carbamide respectively with Nitro-derivatives of Benzene. ROBERT KREMANN and BRUNO PETRITSCHEK (*Monatsh.*, 1917, **38**, 385—404. Compare A., 1905, ii, 307; 1906, ii, 268; 1912, ii, 1151).—The binary systems *p*-toluidine with the three dinitrobenzenes, 2:4-dinitrotoluene and the three nitrophenols respectively, and carbamide with the three

dinitrobenzenes and 2:4-dinitrotoluene respectively, have been investigated by means of time-cooling curves. It is shown in the case of p-toluidine with the three dinitrobenzenes and with 2:4-dinitrotoluene gives no compounds, but only simple eutectics; with m- and p-nitrophenols, a compound is formed in each case. With m-nitrophenol and p-toluidine, the compound produced consists of one molecule of each constituent, whilst with p-nitrophenol, the compound consists of two molecules of p-nitrophenol to one molecule of p-toluidine. In the case of o-nitrophenol and p-toluidine, no compounds are formed, but simply a eutectic. Carbamide does not form any compounds in any of the mixtures examined, and in all cases there are large gaps in the mixture series. As a result of the experiments, the authors state that the tendency to compound formation with the dinitrobenzenes is determined by the residual affinity of the benzene nucleus and not by the affinity of the amino-group, whereas in the case of the nitrophenols the amino-group is the determining factor.   J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XI. Binary Solution Equilibria between Phenol and the Three Isomeric Nitrophenols respectively with the Three Isomeric Phenylene Diamines. Robert Kremann and Bruno Petritschek (*Monatsh.*, 1917, **38**, 405—444. Compare preceding abstract).—By means of cooling curves, the authors have investigated the twelve possible binary systems formed between phenol and the three nitrophenols on the one hand and the three phenylenediamines on the other. The system phenol–p-phenylenediamine gives rise to the compound consisting of one molecule of diamine to two molecules of phenol. This compound forms a eutectic with phenol at 40° and with p-phenylenediamine at 94°. The system phenol–m-phenylenediamine gives rise to a compound made up of three molecules of phenol and two molecules of the diamine; this compound forms a eutectic with phenol at 24° and with diamine at 41°, and has m. p. 52·6°. In the case of the system phenol–o-phenylenediamine, two compounds appear; these consist respectively of four molecules of phenol and one molecule of the diamine, and one molecule of each component. The eutectics in the case of the first compound lie at 28° with phenol and 29° with the second compound. The system p-nitrophenol–o-phenylenediamine forms a single compound composed of two molecules of nitrophenol and one molecule of the diamine (m. p. 87·9°). This compound with nitrophenol has a eutectic at 85·5° and with diamine at 78°. A compound of similar composition is formed in the system p-nitrophenol–m-phenylenediamine; this melts at 119·9°, and its eutectics lie at 102° with nitrophenol and 52·4° with the diamine. In the system p-nitrophenol–p-phenylenediamine, two compounds are found; these have compositions: (*a*) four molecules of nitrophenol to one molecule of the diamine, and (*b*) one molecule of nitrophenol to one molecule of the diamine respectively. The eutectics lie at 109·5° for p-nitrophenol and compound a, 117·5° for compound a and com-

pound b, and 107° for the compound b and the diamine. The systems o-nitrophenol and the three phenylenediamines do not give rise to compounds; the eutectics in these cases lie at 42·5° for p-phenylenediamine, 33·5° for m-phenylenediamine, and 38·8° for o-phenylenediamine. The system m-nitrophenol–m-phenylenediamine gives rise to two compounds, composed of two molecules of nitrophenol and one molecule of the diamine, and one molecule of nitrophenol and one molecule of the diamine respectively. In the system m-nitrophenol–o-phenylenediamine, two compounds are found; these are two molecules of nitrophenol with one molecule of o-phenylenediamine and an equimolecular compound. Similar relationships are found in the system m-nitrophenol–p-phenylenediamine. J. F. S.

A Complete Review of Solutions of Oceanic Salts. III. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1918, **102**, 41—65. Compare A., 1917, ii, 527).—In the previous paper, a graphic representation was devised for the doubled ternary system $(Na_2,K_2,Mg)(Cl_2,SO_4)$ in presence of sodium chloride as a constant solid phase. The diagram took the form of a triangle for any particular temperature, the corners of the triangle corresponding with the three salts $MgCl_2$, $2KCl$, Na_2SO_4. The temperature co-ordinate being perpendicular to the plane of the triangle, the complete diagram took the form of a three-sided prism. Although sodium chloride is always present as a solid phase, the quantity in solution or the quantity of water corresponding with saturation with salt at different temperatures has been hitherto neglected. In the present paper this new factor is taken into account. At first the new variable is considered in connexion with the simple salts represented by the corners of the triangle, and later with respect to the systems associated with the sides. For an interpretation of the numerous diagrams given the original paper must be referred to. [See, further, *J. Soc. Chem. Ind.*, 1918, March.]
E. H. R.

Chemical Kinetics. U. PRATOLONGO (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 182—190).—The author bases on Marcelin's work (Contribution à l'étude de la cinétique physico-chimique, Thesis, Paris, 1914) the essentials of a new thermodynamics of irreversible phenomena. T. H. P.

Effect of Temperature and of Pressure on the Limits of Inflammability of Mixtures of Methane and Air. WALTER MASON and RICHARD VERNON WHEELER (T., 1918, **113**, 45—57).—Theoretical considerations indicate that the effect of increasing the initial temperature of mixtures of inflammable gases with air should be to widen the difference in the composition of the mixtures which correspond with the upper and lower limits of inflammability.

Experiments made with mixtures of methane and air show that the percentage of methane, corresponding with the lower limit,

decreases from 6·00% of methane, when the initial temperature
of the mixture is 20°, to 3·25% for an initial temperature of 700°.
In the case of the higher limit mixture, the percentage of methane
increases slowly with the initial temperature of the mixture up to
about 600°, after which there is a considerable augmentation of
the rate of increase of the methane content. It is suggested that
this is probably due to the disturbing influence of surface com-
bustion of the methane during the interval which elapses between
the introduction of the gas mixture into the heated explosion
vessel and the passing of the igniting spark. In general, the results
obtained for the influence of the initial temperature on the limits
of inflammability agree closely with those obtained by Taffanel
(*Compt. rend.*, 1913, **157**, 593).

Experiments made to determine the influence of pressure on
the composition of the limit mixtures show that the percentage of
methane increases with pressure for both the lower and upper
mixtures. This result is in agreement with previous observations
made by Terres and Plenz (*J. Gasbeleucht.*, 1914, **57**, 990, 1001,
1016, 1025). The smaller effect obtained by these authors in the
case of the upper limit mixtures is presumed to be due to the
circumstance that they did not make use of a sufficiently powerful
source of ignition in order to obtain strictly comparable results.

The lowest pressure at which self-propagation of flame occurs
in mixtures of methane and air was found to be 120 mm. when the
initial temperature was atmospheric. In similar experiments,
Burrell and Robertson (U.S. Bureau of Mines, Technical Paper
No. 121, 1916) obtained a limiting pressure of 300 mm. The differ-
ence between the two results is explicable on the asumption that
the igniting source employed by these authors was not sufficiently
powerful. In these circumstances, their results give merely the
limiting pressure for ignition by a spark discharge of particular
intensity.

The mixtures which correspond with the lowest limiting pres-
sures contain between 8·75 and 9·40% of methane, these numbers
being derived from observations in which the initial temperatures
were 20°, 250°, and 500°.   H. M. D.

The Saponification of Fats. II. J. P. TREUB (*Proc. K. Akad.
Wetensch. Amsterdam*, 1918, **20**, 343—357. Compare A., 1917,
ii, 528).—From a mathematical discussion of the ideal case in
which the saponification of a triglyceride takes place in solution,
the ester groups being equivalent and no complications arising, it
is shown that the relative concentration of free glycerol at any
moment is equal to the third power of the relative concentration
of the free fatty acid, in the case of stagewise saponification, that
is, passage through the di- and mono-glycerides. The same holds
good for the ideal case of esterification. The experimental results
obtained when trilaurin is saponified with strong sulphuric acid
show only very slight deviations from this rule, the deviations being
due to the fact that the three ester groups are not perfectly equi-
valent. Rather greater deviations are found in the esterification of

lauric acid and glycerol by strong sulphuric acid. [See also *J. Soc. Chem. Ind.*, 1918, March.]   W. G.

Dynamics of Nitrile Formation from Acid Anhydrides and Amides. I. Investigation of the Reaction $O(COPh)_2 + COPh \cdot NH_2 \longrightarrow 2Ph \cdot CO_2H + PhCN$, by Methods based on the Phase Rule. ROBERT KREMANN and MAX WENZING (*Monatsh.*, 1917, **38**, 445—456).—In a series of experiments designed for the investigation of the binary mixture, benzoic anhydride–benzamide, the authors found that the temperature of the primary crystallisation varied with the time during which the mixture had been heated and also with the temperature. This they were able to show was due to the reaction $O(COPh)_2 + COPh \cdot NH_2 \longrightarrow 2Ph \cdot CO_2H + PhCN$. To follow this reaction, mixtures of the four substances taking part were made in a number of different proportions, commencing with 100% of the substances on the right hand side of the equation and ending with 100% of the substances on the left hand side, but always so that the molecular ratio of the benzoic acid to the benzamide was 2:1 and that of the benzoic anhydride to the benzamide was 1:1. These mixtures were rapidly heated to 98° and then allowed to cool, and the temperature of primary crystallisation noted. The crystallisation temperatures were plotted against the composition and an analytical curve produced, which on the assumption that no chemical change had occurred gives the composition of any mixture, in which the proper ratios of the two sides of the equation are maintained, directly from the temperature of its primary crystallisation. The reaction was then studied: quantities of benzoic anhydride and benzamide in molecular proportions were mixed in a closed vessel heated to 98° or 123°, and the temperature of primary crystallisation measured at stated intervals of time (one to one hundred hours), and from the analytical curve the progress of the reaction ascertained. It is shown that the reaction is bimolecular, and at 98° has a value $k = 0.053$, whilst at 123° $k = 0.24$. The temperature-coefficient is therefore 1·8 for 10°. It is shown also that the reverse reaction does not take place to the extent of more than 1%.   J. F. S.

Influence of Carbon Monoxide on the Velocity of Catalytic Hydrogenation. EDWARD BRADFORD MAXTED (*Trans. Faraday Soc.*, 1917, **13**, 36—42).—Measurements have been made of the rate of absorption of hydrogen by olive oil at 180° in presence of small quantities of carbon monoxide. The absorption vessel, containing the oil and a nickel catalyst, was connected to the gas-measuring tube by rubber tubing, and was adjusted so that the contents could be continuously and thoroughly shaken during the progress of the absorption.

Comparative experiments with pure hydrogen and with hydrogen containing from 0·25 to 2% of carbon monoxide show that the rate of hydrogenation is very considerably reduced by these quantities of carbon monoxide. The curve obtained by plotting the hydrogen absorption for a given interval of time against the per-

centage of carbon monoxide in the hydrogen is convex towards the origin, indicating that the retarding influence of successive increments in the carbon monoxide content decreases with increase in the quantity of the poisonous gas.

Apart from the poisoning effect of the carbon monoxide, the admixture of this gas dilutes the hydrogen, but this effect can be readily calculated and allowed for.　　　　　　　　　H. M. D.

Hydrogenation under the Influence of Colloidal Catalysts and how to account for this Process. J. Böeseken and H. W. Hofstede (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 424—434).—The question of the mechanism of colloidal metal catalysts in hydrogenation processes is discussed and the results of observations are recorded on the rate at which hydrogen is absorbed by solutions of cinnamic acid, cinnamic esters, and ethyl undecenoate in presence of colloidal palladium. These results are not sufficiently regular to admit of mathematical treatment, and the authors infer that the normal course of the reaction is disturbed by impurities in the hydrogen, by coagulation of the catalyst, and by other unknown factors. [See *J. Soc. Chem. Ind.*, 1918, March.]　　　　　　　　　　　　　　　　　H. M. D.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for different Elements in Connexion with the Periodic System. V. The Elements of the Carbon and Titanium Groups. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 492—504. Compare A., 1916, ii, 386, 610; 1917, ii, 67).—The methods previously described have been applied to the calculation of the values of b and $\sqrt{a}$ for the elements of the carbon and titanium groups. The critical data for these elements are, of course, not known, but the values of b can be obtained from the compounds, for which in certain cases the requisite data are available. The chief result to which the author's calculations lead is that the value of $\sqrt{a}$ must be very large, ranging from $0\cdot32$ for carbon to $0\cdot40$ for lead. This is supposed to indicate that the attractive forces measured by $\sqrt{a}$ are those of the free atoms.

The estimated values of $\sqrt{a}$ and b and also of the critical temperature and pressure are recorded in tables.　　　　　H. M. D.

The Fundamental Values of the Quantities b and $\sqrt{a}$ for different Elements in Connexion with the Periodic System. VI. The Alkali Metals. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 505—519. Compare preceding abstract).—An attempt is made to estimate the values of b and $\sqrt{a}$ for the alkali metals, the approximate value of the critical temperature required in the calculations being derived from the melting points and boiling points. The physical properties of the alkali metals necessitate the assumption of high values for the attraction constant, and this is assumed to be connected with the existence of these elements in the atomic condition. The estimated

ii. 74

values of the critical data and of b and $\sqrt{a}$ are recorded in tabular form.   H. M. D.

Considerations on the Nature of Chemical Affinity and of the Valency of Atoms G. CIAMICIAN and M. PADOA (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 165—173).—The bearing of the results of recent work on the structure of the atom and on valency is discussed.   T. H. P.

Vacuum Balance Cases. BERTRAM BLOUNT and WILLIAM H. WOODCOCK (T., 1918, **113**, 81—84).—Attempts have been made to construct a vacuum balance case of gun-metal. On account of the porosity of the metal, it was not found possible to reduce the rate of leakage much below that represented by 0·01 mm. per hour.

Better results were obtained with a glass case consisting of a large bell-jar with a side tubulus, through which the rider is controlled by an arrangement which is commonly made use of in the ordinary glass hypodermic syringe. A balance case constructed on these lines has been found to give satisfactory results. By means of a Gaede pump it can be exhausted to 0·001 mm. and the vacuum can be maintained for more than an hour.   H. M. D.

Method for Preventing Salts from Creeping over the Sides of Evaporating Dishes. W. O. ROBINSON (*J. Amer. Chem. Soc.*, 1918, **40**, 197).—Creeping of salts can be prevented by painting a strip, about 6—7 mm. wide, round the inner rim of the dish with collodion. The film contains no non-volatile residue and can be easily burnt off.   H. M. D.

Lecture Experiment on the Vapour Pressure of Solutions. H. S. VAN KLOOSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 193—195). —A simple apparatus is described for demonstrating the lowering of the vapour pressure of a volatile liquid on the addition of a foreign non-volatile substance. It consists of an outer glass tube, in which the pure liquid is boiled, and an inner tube containing the solution. The inner tube is constricted somewhat about the middle of its length, and at its lower end is sealed on to a narrow tube, which is bent round to form a U with the wider tube, and is used as a gauge tube. The constriction serves to close the inner tube, when all the air has been removed, and this is conveniently effected by a rubber cork attached to a glass rod. When the outer tube is closed and the liquid boils,, vapour passes through the solution viâ the gauge tube, and when the air has been displaced the inner tube is closed by the rubber stopper. The level of the solution in the gauge tube is then found to be less than that in the wider tube.   H. M. D.

Preparation of Argon as a Lecture Experiment. W. P. JORISSEN (*Chem. Weekblad*, 1917, **14**, 1151—1153).—A description of an apparatus for demonstrating the extraction of argon

from air, the oxygen being absorbed by phosphorus, and the nitrogen by a mixture of magnesium-powder, fresh quick-lime, and sodium.   A. J. W.

Inorganic Chemistry.

The Crystalline System and the Axial Ratio of Ice.
F. RINNE (*Ber. K. Sachs. Ges. Wiss. Math-phys. Klasse*, 1917, **69**,
57—62; from *Chem. Zentr.*, 1917, ii, 671. Compare *ibid.*, i, 452).
—Using the apparatus described earlier, the statement of Nordens-
kiöld that ice is hexagonal–bipyramidal (hexagonal–hemimorphic,
$a:c=1:1\cdot6$) is confirmed. This result is regarded as supporting
the author's law of isotypism, according to which ice follows the
magnesium type.   D. F. T.

Black Phosphorus. II. A. SMITS, G. MEYER, and R. TH.
BECK (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 392—393.
Compare A., 1916, ii, 185).—Experiments in which black and
violet phosphorus were heated for prolonged periods at 480° and
450° indicate that the black modification is metastable at these
temperatures, and in presence of 1% of iodine as catalyst is trans-
formed into the violet form. Mixtures of violet and black phos-
phorus in the ratio 4:1 heated for fourteen weeks at 380° showed
complete transformation of the black into the violet form, but no
appreciable change took place when the proportion of violet to
black was 1:4. [See *J. Soc. Chem. Ind.*, 1918, March.]
                                                                  H. M. D.

The Thermal Dissociation of Metaphosphoric Acid. D.
BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **102**, 34—40).—The author
studies the formation and thermal dissociation of metaphosphoric
acid by heating orthophosphoric acid for varying lengths of time in
a pear-shaped gold flask having a long neck. A current of dry air,
led into the flask through a gold tube, serves to carry away any
water-vapour formed, whilst the volatilised metaphosphoric acid and
phosphoric oxide condenses in the neck of the flask. At the end of
an experiment the flask is closed, weighed, and the residue analysed
by estimating phosphoric oxide by the method of Schmitz. The
product always contains less water than that required for metaphos-
phoric acid, the deficiency being greater the more prolonged the
heating. The thermal dissociation of metaphosphoric acid in the
gaseous state is therefore established. The results of those ob-
servers who have obtained metaphosphoric acid containing excess
of water are to be explained by insufficient heating or by the
presence of impurities in the phosphoric acid used (compare Holt
and Myers, T., 1913, **103**, 532—536). The dehydration of ortho
phosphoric acid solutions by heating does not take place in definite

stages, but is influenced by the rate of heating and by the vapour
tensions of water and phosphoric oxide.   Even at 260—300° phos-
phoric acid volatilises with the water in appreciable quantities.
The composition of the residue depends on the temperature and
duration of heating.   [Compare *J. Soc. Chem. Ind.*, 1918, March.]
                                                          E. H. R.

The Existence of Basic Calcium Carbonates.   ED. DONATH
and A. LANG (*Österr. Chem. Zeit.*, 1917, [ii], **20**, 175—176; from
Chem. Zentr., 1917, ii, 672).—When brought into contact with
water and lime, calcium carbonate becomes hardened, due to a
fixation of part of the lime; this result is adduced as evidence of
the probable existence of basic carbonates of calcium (compare
Busvold, A., 1917, ii, 207).   D. F. T.

Glucinum Nitride.   A. C. VOURNASOS (*Bull. Soc. chim.*, 1917,
[iv], **21**, 282—288.   Compare A., 1911, ii, 600; 1913, i, 25).—
Glucinum nitride may be obtained by the direct action of cyano-
gen on glucinum at 800°.
The partial oxidation of a cyanide or of a carbide in the pres-
ence of nitrogen will in certain cases yield nitrides.   Thus if zinc
or copper cyanide or calcium carbide is heated with ammonium
nitrate, the corresponding nitride is formed: $3Zn(CN)_2 +$
$12NH_4NO_3 = Zn_3N_2 + 6CO_2 + 14N_2 + 24H_2O$.   Barium cyanamide
similarly reacts with ammonium nitrate to give barium nitride.
[See also *J. Soc. Chem. Ind.*, 1918, March.]   W. G.

A Silica-Glass Mercury Still.   J. C. HOSTETTER and R. B.
SOSMAN (*J. Washington Acad. Sci.*, 1918, **8**, 11—15).—Vacuum
mercury stills made of ordinary or combustion glass are liable to
collapse when slightly overheated.   This has led to the construction
of a silica-glass still, the design of which is of the simplest possible
kind, in order to minimise the difficulties connected with the work-
ing of the fused silica.   The distillation chamber is heated electri-
cally and the pressure reduced to less than 10 mm.   H. M. D.

Mercury Ammonia Compounds.   I.   MURIEL CATHERINE
CANNING HOLMES (T., 1918, **113**, 74—79).—By digesting infusible
precipitate at 100° with solutions nearly saturated with respect to
ammonium chloride and containing varying quantities of mercuric
chloride, and examining the crystals which separate on cooling, it
has been found that the product consists of the compound
$3HgCl_2,2NH_3$ or of $HgCl_2,2NH_3$.   There is no evidence of the
formation of any compound of intermediate composition.
The product obtained under similar conditions by using solutions
nearly saturated with mercuric chloride and variable small amounts
of ammonium chloride has the composition $HgCl_2,NH_2 \cdot HgCl$.
This compound has previously been obtained by Strömholm (A.,
1906, i, 935; *Zeitsch. anorg. Chem.*, 1908, **57**, 72).   H. M. D.

Electrolysis of Solutions of the Rare Earths.   III.   L. M.
DENNIS and A. B. RAY (*J. Amer. Chem. Soc.*, 1918, **40**, 174—181).
The fact that the electrolysis of solutions of rare earth salts leads

to the fractional precipitation of the rare earth hydroxides (compare A., 1915, ii, 775) has been attributed to the action of the hydroxyl ions set free at the mercury cathode, the hydroxide of the weakest base being precipitated first. In the expectation that vigorous stirring of the mercury surface would facilitate the fractionation, experiments have been made with neutral solutions of the nitrates of the rare earths of the yttrium and erbium groups, the average atomic weight of the metal being 106·95. The hydroxides precipitated at different stages were removed and the average atomic weight of the metal in each fraction determined.

Comparing the results obtained in two series of electrolytes, in one of which the cathode was vigorously, and in the other slightly agitated, it is found that vigorous stirring causes a more rapid segregation of the earths of higher atomic weight in the early fractions and a better concentration of the earths of lower atomic weight in the last fractions.

Other experiments in which neutral solutions of the nitrates of the rare earths and thorium were electrolysed show that fractionation occurs, the thorium being concentrated in the early fractions. [See also *J. Soc. Chem. Ind.*, 1918, March.]   H. M. D.

A Thermoelectric Method for the Study of the Allotropic Transformations of Metals. R. DURRER (*Stahl und Eisen*, 1917, **37**, 430—431; from *Chem. Zentr.*, 1917, ii, 672. Compare Benedicks, A., 1916, ii, 172).—After a description of the apparatus used by Benedicks, a statement is made that the decision of the latter with respect to the discontinuity at the point A_3 of the curve for iron and the absence of discontinuity at the point A_2 is based on insufficient material.   D. F. T.

Iso- and Hetero-poly Acids. XV. Heteropolytungstates and some Heteropolymolybdates. ARTHUR ROSENHEIM and JOHANNES JAENICKE (*Zeitsch. anorg. Chem.*, 1917, **101**, 235—275. Compare this vol., 19).—In this paper is given the new experimental data which the authors have used in the development of their theory of the constitution of the heteropoly acids. The acids of the fundamental type have the constitution expressed by the formula $H_{12-n}[R^n(M_2O_7)_6]$, where R is the non-metallic element and M the metallic. These acids form two series of hydrates, one series crystallising in quadratic octahedra with $28H_2O$, the other in rhombohedra with $22H_2O$. They are the most stable of the heteropoly acids and are formed in presence of excess of the metallic acid. The 8- and 9-basic acids show isomerism of a type not understood.

12-*Borotungstic acid*, $H_9[B(W_2O_7)_6],28H_2O$, forms crystals of two kinds, large, transparent octahedra, m. p. 45—51°, and slender needles. A lower hydrate with $10H_2O$ was isolated. An *iso*-12-*borotungstic acid*, $H_9[B(W_2O_7)_6],22H_2O$, was obtained in the form of hexagonal, bipyramidal crystals.

12-*Silicomolybdic acid*, $H_8[Si(Mo_2O_7)_6],28H_2O$, forms transparent octahedra, which melt gradually at 47—55° to a uniform liquid.

Crystallised from hot nitric acid, it forms a lower hydrate with $14H_2O$.

12-Silicotungstic acid forms both quadratic and rhombohedral hydrates with $28H_2O$ and $22H_2O$ respectively. The transition point, determined by the dilatometer method, is at $28.5°$. In addition, a hydrate with $15H_2O$ was obtained.

Iso-12-silicotungstic acid, $H_8[Si(W_2O_7)_6],20H_2O$, forms triclinic prisms.

12-Phosphomolybdic acid was obtained in yellow, octahedral crystals of the composition $H_7[P(Mo_2O_7)_6],28H_2O$, and by crystallisation from hot nitric acid the hitherto unknown hydrate with $22H_2O$ was obtained in small, yellow, probably rhombohedral tables. The conductivity at $25°$ was studied, and also the course of neutralisation by means of conductivity measurements.

12-Phosphotungstic acid forms crystals of the normal type with $28H_2O$. In presence of traces of acid these break down into minute rhombohedra of the hydrate with $22H_2O$, melting at 89—94° to a homogeneous liquid. The highest metallic salts which could be prepared were tribasic, for example, $Ba_3H_8[P(W_2O_7)_6]_2,54H_2O$ and $Na_3H_4[P(W_2O_7)_6],13H_2O$, but in the guanidine salt,

$$(CN_3H_5)_7H_7[P(W_2O_7)_6]_2,12H_2O,$$
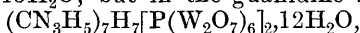
half the hydrogen is replaced.

12-Arsenotungstic acid could only be obtained in the form of its ammonium salt, $(NH_4)_3H_4[As(W_2O_7)_6],4H_2O$.

The unsaturated mono-nucleic heteropoly acids are of the type $H_{12-n}[R^nO(M_2O_7)_5]$, their basicity being the same as that of the saturated acids.

10-Silicotungstic acid was obtained in the form of a potassium salt, badly formed, cube-like crystals of the composition

$$K_7H[SiO(W_2O_7)_5],11H_2O.$$
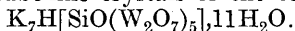
The corresponding guanidine salt contains $9H_2O$.

The bi-nucleic heteropoly acids form two groups, the $1:11$ acids having an outer bridge,

$$H_7[R^n \cdot OH \cdot (M_2O_7)_5] \cdot M_2O_7,[R^n \cdot OH \cdot (M_2O_7)_5]H_7,.$$
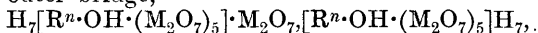
whilst the $1:9$ (luteo) acids have an inner bridge,

$$H_{11-n}[(M_2O_7)_4R^nO \cdot M_2O_7 \cdot R^nO \cdot (M_2O_7)_4]H_{11-n}.$$
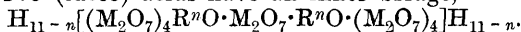
The acids of the last type, it is suggested, are in tautomeric equilibrium with the form

$$H_{10-n}[(M_2O_7)_4R^nOH \cdot M_2O_7 \cdot R^nOH(M_2O_7)_4]H_{10-n}.$$
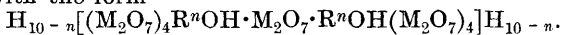
They are always formed in presence of excess of the metalloid acid.

11-Phosphotungstates are formed at an intermediate stage in the decomposition of 12-phosphotungstic acid by strong bases. They are stable salts which can be readily prepared from the barium salt, to which the constitution

$$Ba_7[P(OH)(W_2O_7)_5] - W_2O_7 - [(W_2O_7)_5(OH)P]53H_2O$$
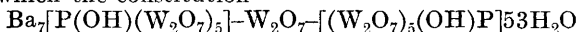
is given. Strong mineral acids bring about decomposition of the 11-phosphotungstates with formation of 12- and 2:21-phosphotungstates. The 11-*arsenotungstates* are completely analogous to the corresponding phosphotungstates.

9-Phosphotungstic acid, $P_2O_5,18WO_3,42H_2O$, forms thin, six-sided tables, which are very readily soluble and melt at 28°. All

attempts to prepare salts of higher basicity than 5 failed, and it is concluded that the constitution of the acid must be represented by the formula

$$H_5[P(OH)(W_2O_7)_4-W_2O_7-(W_2O_7)_4(OH)P]H_5,36H_2O.$$
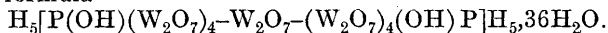
A study of the conductivity and neutralisation curves points to the same conclusion.

The silver salt, $5Ag_2O,P_2O_5,18WO_3,34H_2O$, is precipitated as yellow, amorphous flakes which quickly crystallise. It is almost insoluble. The corresponding guanidine salt, with $18H_2O$, forms bright yellow aggregates of small tables and is only slightly soluble.

9-*Arsenotungstic acid* corresponds exactly with luteophosphotungstic acid. Only the tribasic potassium and ammonium salts were prepared, these having similar properties to the tribasic salts of 9-phosphotungstic acid.

Among the more complex heteropoly acids, the authors have studied 2:21-phosphotungstic acid, 2:17-phospho- and 2:17-arsenotungstic acids. They probably contain four non-metallic acid nuclei, but no constitutional formulæ have yet been suggested for them. The preparation and properties of a number of salts of these acids are described. E. H. R.

Mineralogical Chemistry.

Amblygonite–Tin Deposits at Caceres, Spain. W. T.
Dörpinghaus (*Jahrb. Min.*, 1917, i, Ref. 326—328; from *Archiv
Lagerstättenforschung*, 1914, **16**, 49 pp.).—Veins containing
amblygonite and cassiterite intersect Silurian and Devonian slates
in the neighbourhood of the well-known phosphate veins of
Estremadura. The average composition of the amblygonite is given
under I. Associated minerals are pyrophyllite (anal. II) and a
soda-muscovite (III).

	SiO_2.	P_2O_5.	SO_3.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.
I.	—	46·35	—	34·29	0·79	—	—
II.	67·01	trace	trace	17·93	0·06	—	—
III.	45·78	trace	0·08	36·49	0·15	0·08	0·11

	K_2O.	Na_2O.	Li_2O.	H_2O.	F.
I.	—	1·60	8·87	5·16	3·00
II.	6·27	2·23	—	6·69	—
III.	8·41	3·25	—	5·15	—

L. J. S.

Celestite from Galicia. Stefan Kreutz (*Jahrb. Min.*, 1917, i,
Ref. 269—277; from *Abh. Akad. Wiss. Krakau*, 1915, **55**, [*A*],
1—24).—An account is given of the minerals (aragonite, rock-salt,
gypsum, celestite, calcite, and dolomite) found in the salt-clays
which are worked for ozocerite and sulphur in the mining district

of Pomiarki, near the village of Truskawiec in Galicia. A crystal-lographic description is given of the celestite; analysis gave:

SrO.	BaO.	CaO.	SO$_3$.	Ign.	Total.	Sp. gr.
54·41	0·69	0·67	43·54	0·22	99·53	3·968

corresponding with SrSO$_4$ 97·38, CaSO$_4$ 1·64, BaSO$_4$ 0·98.

Mixed crystals of these sulphates are discussed, and the fact that the minerals celestite, barytes, and anhydrite always contain a predominance of one metal is commented upon.   L. J. S.

The Existence of Bischofite Deposits and the Secondary Transformations of the Zechstein Potassium Salts. M. RÓZSA (*Zeitsch. anorg. Chem.*, 1917, **101**, 276—284. Compare A., 1916, ii, 257, 335; 1917, ii, 97, 214).—Fresh arguments are put forward in support of the author's contention that bischofite did not form a primary deposit, and therefore could not have participated in the secondary metamorphoses of the salt deposits. The carnallite–kieserite salts of the 16 metres thick "principal" salt layers are the primary products. The mean composition of five borings through this deposit gave carnallite 56%, kieserite 13·3%, rock-salt 28·7%. The kieserite–carnallite layers are less rich in carnallite. The origin of this carnallite can be explained without the assumption of a primary bischofite deposit, on the supposition that the magnesium chloride appears as a decomposition product of the "principal" salt deposit.

The thermal or hydrothermal decomposition of kainite into kieserite and carnallite has been studied from the van't Hoff equilibrium diagram, and it is concluded from the relative proportions of these two salts in the "principal" salt deposits that the last could not have been produced by the decomposition of kainite. The occasional transformation of the "principal" deposits into a hard-salt rich in langbeinite can be explained qualitatively, but quantitative data are wanting. [See also *J. Soc. Chem. Ind.*, 1918, March.]   E. H. R.

Rock-forming Minerals from the Tatra Mountains. W. PAWLICA (*Jahrb. Min.*, 1917, i, Ref. 278—282; *Bull. Acad. Sci. Cracovie, Cl. sci. math. nat.*, [A], 1915, 52—76).—Thirteen detailed analyses are given of minerals (muscovite, biotite, orthoclase, oligoclase, amphibole, garnet, and tourmaline) isolated from granite, pegmatite, and gneiss.   L. J. S.

Analytical Chemistry. .

Accurate Method for taking Aliquots of a Standard in Standardising Solutions. C. F. MILLER (*J. Amer. Chem. Soc.*, 1917, **39**, 2388).—About five times as much of the standard substance is weighed out and dissolved in a quantity of water slightly

exceeding five times the capacity of the pipette to be used in taking the aliquot portions. (This pipette need not be standardised.) Five portions of the solution are now pipetted into separate vessels, and the remainder of the solution, together with the rinsings from the pipette, is transferred to a tared platinum basin, evaporated, the residue dried, and weighed. A simple calculation gives the quantity of substance taken for each titration. The method can be used only for such substances as sodium carbonate, sodium oxalate, etc., which are soluble, and separate from their solution in a weighable form on evaporation.   W. P. S.

A General Method for the Analysis of Gaseous Mixtures. PAUL LEBEAU and A. DAMIENS (*Ann. Chim.*, 1917, [ix], **8**, 221—264).—A more detailed account of work already published (compare A., 1913, i, 437; ii, 253, 349, 700).   W. G.

The McLean-Van Slyke Iodometric Method for the Titration of Small Amounts of Haloids. Its Application to Chlorides. ROBERT F. McCRACKEN and MARY D. WALSH (*J. Amer. Chem. Soc.*, 1917, **39**, 2501—2506. Compare A., 1915, ii, 479).— When the titration in this method is made very slowly, a blue coloration which might be mistaken for the end-point sometimes develops before the titration is complete; this coloration, however, disappears gradually as the end-point is approached. The end-point can be obtained in a clear solution by adding a further quantity of starch just before the titration is commenced. The method yields trustworthy results. [See, further, *J. Soc. Chem. Ind.*, 1918, 6A.]   W. P. S.

Applications of Gas Analysis. IV. The Haldane Gas Analyser. YANDELL HENDERSON (*J. Biol. Chem.*, 1918, **33**, 31—38). —Modifications of Haldane's apparatus for the estimation of carbon dioxide in air and in blood are described, by means of which the apparatus may be more readily taken apart and cleaned. A simpler form of the apparatus suitable for teaching purposes is also illustrated. [See also *J. Soc. Chem. Ind.*, 1918, March.]   H. W. B.

Applications of Gas Analysis. V. The Gases of the Blood. YANDELL HENDERSON and ARTHUR H. SMITH (*J. Biol. Chem.*, 1918, **33**, 39—46. Compare preceding abstract).—The authors describe a modification of Barcroft and Haldane's method, in which the oxygen from 1 c.c. of the blood is liberated by the action of potassium ferricyanide in a special " diffusion tube," which is subsequently rotated horizontally. During the rotation, the contents of the tube spread in a thin film along the walls and allow complete diffusion of the liberated oxygen into the air of the tube to occur. The excess of oxygen in the air is then estimated by means of the analyser previously described (*loc. cit.*). Carbon dioxide in the blood is similarly estimated after treatment with tartaric acid, a correction being made for the solubility of carbon dioxide in acidified solutions of blood.   H. W. B.

Gasometric Estimation of the Oxygen and Hæmoglobin of Blood. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1918, **33**, 127—132. Compare A., 1917, ii, 422).—The apparatus previously described for the estimation of carbon dioxide in the blood is used with a similar technique for the estimation of oxygen. The oxygen is liberated from combination with hæmoglobin within the apparatus by the addition of ferricyanide, is extracted in a vacuum, and measured at atmospheric pressure, a few minutes sufficing for an accurate estimation.   H. W. B.

Rapid Characterisation of the Sulphuric Ion in Insoluble Sulphates. Application to the Identification of this Ion in General. G. DENIGÈS (*Bull. Soc. chim.*, 1918, [iv], **23**, 36—39).— The presence of the sulphuric ion in insoluble sulphates, such as those of lead, mercurous mercury, calcium, strontium, and barium, may readily be shown by adding to the sulphate a 10% solution of mercuric nitrate in nitric acid (1 in 100). Turpeth mineral is formed, and may be detected, if necessary, microscopically. Calcium and mercurous sulphates give the reaction immediately in the cold, strontium and lead sulphates only slowly, and barium sulphate only on boiling. In a complex mixture, the sulphate may be first precipitated as barium sulphate and then detected as described. [See also *J. Soc. Chem. Ind.*, 1918, March.]   W. G.

The Adaptation of Truog's Method for the Estimation of Carbon Dioxide to Plant Respiration Studies. A. M. GURJAR (*The Plant World*, 1917, **20**, 288—293; from *Physiol. Abstr.*, 1918, **2**, 641).—In the original paper an apparatus is described for the estimation of carbon dioxide by Truog's method, the gas being absorbed in a known volume of $N/4$-barium hydroxide solution, and the residual hydroxide titrated back with standard acid. The modification consists in the use of an automatic pipette for measuring and transferring the barium hydroxide solution without allowing it to come into contact with the air. There is also an arrangement for rendering the wash-water free from carbon dioxide without disconnecting the reservoir.   W. G.

Use of Sodium Paratungstate in the Estimation as Oxide of the Metal in Cyanides. S. B. KUZIRIAN (*J. Amer. Chem. Soc.*, 1917, **39**, 2356—2358. Compare A., 1913, ii, 865).— Cyanides, when heated with sodium paratungstate in the presence of an oxidising substance (ammonium nitrate) lose their acid radicle, leaving a residual oxide in a definite and stable form for weighing together with the paratungstate. [See, further, *J. Soc. Chem. Ind.*, 1918, 30A.]   W. P. S.

Estimation of Sodium and Potassium. F. H. McCRUDDEN and C. S. SARGENT (*J. Biol. Chem.*, 1918, **33**, 235—241).—Sodium and potassium are separated from other compounds as the combined chlorides, and the amount of each is calculated from the chlorine content of a known weight of the mixture. The authors

show that when the McLean-Van Slyke method is employed for estimating the chlorine, the probable error in the estimation of the sodium increases as the ratio of sodium to potassium decreases, and amounts usually to about 1%.　　　　　　　　　　　　　　　　H. W. B.

New Hydrogen Electrode for the Electrometric Titration of the Alkaline Reserve of Blood Plasma and other Frothing Fluids.

J. F. McClendon (*J. Biol. Chem.*, 1918, **33**, 19—29).— The new electrode vessel is attached to a horizontal spindle in such a way as to permit the introduction at the free end of acid and of hydrogen during rotation without disconnection from the potentiometer. The addition of $N/10$-hydrochloric acid to the plasma is continued until the hydrogen-ion concentration is that of water ($pH = 7{\cdot}00$ at 23°). The amount of acid required is a measure of the alkaline reserve of the blood.　　　　　　　　　　　　H. W. B.

Volumetric Method for the Estimation of Calcium.

J. Grossfeld (*Chem. Zeit.*, 1917, **41**, 842).—The calcium is precipitated from a solution slightly acidified with phosphoric acid by the addition of a definite quantity of ammonium oxalate, the calcium oxalate is then separated by filtration through a "kieselguhr filter-paper," and the excess of ammonium oxalate is titrated, with permanganate, in an aliquot portion of the filtrate. [See, further, *J. Soc. Chem. Ind.*, 1918, 76A.]　　　　　　W. P. S.

Identification and Estimation of Lead in Water.

Robert Meldrum (*Chem. News*, 1918, **117**, 49—50).—In the colorimetric estimation of lead by means of hydrogen sulphide, it is essential that the standard or comparison solution be prepared with the same water free from lead. The colouring matter in the water and the proportion of saline constituents influence the intensity of the coloration due to lead sulphide, the difference in some cases amounting to 100%. When distilled water is used for the standard solution, the lead may be underestimated to the extent of 33%. [See, further, *J. Soc. Chem. Ind.*, 1918, March.]　　　　W. P. S.

A New Method of Estimating Copper.

James Moir (*J. Chem., Met., Min. Soc. S. Africa*, 1917, **18**, 133—135).—The sample is dissolved in concentrated nitric acid and the copper converted into faintly acid cupric acetate either by the usual method or by adding carbamide, boiling, nearly neutralising with sodium hydroxide, and adding sodium acetate. A slight excess of sodium thiosulphate is added to the solution, followed immediately by an excess of potassium thiocyanate. The precipitated copper thiocyanate is filtered through filter-pulp and washed, the filtrate is diluted, sulphuric acid and a small quantity of starch solution are added, and the excess of thiosulphate is titrated with $N/10$-iodine solution. [For details, see *J. Soc. Chem. Ind.*, 1918, March 15th.]
　　　　　　　　　　　　　　　　　　　　　　　　T. F. B.

Colorimetric Estimation of Manganese by Oxidation with Periodate. HOBART H. WILLARD and LUCIEN H. GREATHOUSE (*J. Amer. Chem. Soc.*, 1917, **39**, 2366—2377).—Manganese salts are readily oxidised to permanganate by heating with an alkali periodate in acid solution. The quantity of free sulphuric acid present must be sufficient to prevent the precipitation of manganic periodates or oxides; a high concentration of acid, prolonged heating, and the presence of ammonium salts are without effect on the results. Traces of chloride do not interfere, and the common metals, if they do not form coloured ions, may be present. Reducing substances must be removed previously by treatment with nitric acid; phosphoric acid should be·added if much iron is present. The quantity of permanganate formed is estimated colorimetrically. [See, further, *J. Soc. Chem. Ind.*, 1918, 41A.]

W. P. S.

Use of Cupferron (Ammonium Salt of Nitrosophenylhydroxylamine) in : I. The Quantitative Separation of Zirconium, Titanium, Iron, Manganese, and Aluminium. II. The Analysis of Zircon and Baddeleyite. JAMES BROWN (*J. Amer. Chem. Soc.*, 1917, **39**, 2358—2366. Compare Thornton and Hayden, A., 1914, ii, 779).—Cupferron reagent may be used for the precipitation and separation of iron, titanium, and zirconium from aluminium and manganese. The precipitation is made from a sulphuric acid solution. The iron, titanium, and zirconium are then separated from one another by the use of standard methods, and the aluminium and manganese are estimated after the excess, of cupferron has been destroyed by treatment with concentrated nitric acid. The method yields trustworthy results either with mixtures of the pure salts or with minerals containing the elements· mentioned. [See, further, *J. Soc. Chem. Ind.*, 1918, 41A.]

W. P S.

Reagents for Use in Gas Analysis. VII. The Estimation of Benzene Vapour. R. P. ANDERSON (*J. Ind. Eng. Chem.*, 1918, **10**, 25—26).—A method is proposed for the estimation of benzene vapour in gas in which a measured quantity of gas containing benzene vapour is placed in contact with benzene in a special apparatus, and the increase in volume read. By determining what the increase would have been had there been no benzene vapour present, the amount of benzene vapour present can be estimated. A standard apparatus has not yet been produced.

L. A. C.

Estimation of Phenol in the Presence of the Three Cresols. G. W. KNIGHT, C. T. LINCOLN, G. FORMANEK, and H. L. FOLLETT (*J. Ind. Eng. Chem.*, 1918, **10**, 9—18).—From a series of determinations of the specific gravities and solidifying points of a number of mixtures of pure phenol and pure *o*-, *m*-, and *p*-cresols, the authors have devised a method for determining the percentage of phenol present in unknown mixtures of these compounds.

Details are given for carrying out the method and obtaining the necessary measurements for solving the equation :

Per cent. phenol $= 100X$ $[(T_o - T_{so})(0\cdot366 + 0\cdot702L_s) +$
$$(G_{so} - G_o)(2970 - 609L_s)]/30\,W.$$

where $L_s = \{1000(G_p - G_{sp})\}/\{T_p - T_{sp}\} - 0\cdot842$; G_p and $G_{sp} = D_{45}^{45}$ of phenol used and phenol + distillate mixture respectively; G_o and $G_{so} = D_{25}^{25}$ of o-cresol used and o-cresol + distillate mixture respectively; T_p, T_{sp}, T_o, and $T_{so} =$ solidifying points of the phenol, phenol + distillate mixture, o-cresol used and o-cresol + distillate mixture respectively; $X = $ wt. of total distillate below $197°$; $W = $ wt. of sample used.

This equation does not give absolutely accurate results with all possible mixtures of the three isomerides, or where both o-cresol and m-cresol are present and p-cresol is absent or present only in very small quantities, the results in this case being too low. The error increases as o-cresol increases and p-cresol decreases, being greatest where p-cresol is absent and more than 50% of m-cresol and less than 50% of o-cresol is present. In all cases ordinarily met with in commercial practice, however, the probable error would amount to only a few tenths per cent. [See, further, *J. Soc. Chem. Ind.*, 1918, 85ᴀ.] L. A. C.

Estimation of Pentose in Urine. G. TESTONI (*Policlinico*, 1917, **24**, 641; from *Physiol. Abstr.*, 1918, **2**, 598).—Ten c.c. of urine are decolorised by heating with blood charcoal and filtered. The filtrate is evaporated to 5 c.c., and to it is added 9 c.c. of a warm $0\cdot25\%$ solution of phloroglucinol in glacial acetic acid and 1 c.c. of hydrochloric acid. The mixture is allowed to remain at $50°$ for half an hour, when the characteristic colour will have appeared. A quantitative estimation may be made by means of a colorimeter. The method is applicable to diabetic urine. If pentose is the only sugar present, the filtrate from the decolorising process need not be evaporated. W. G.

Estimation of Dextrose in Urine. J. J. GURTOV (*Med. Record, New York*, 1917, **92**, 502—503; from *Physiol. Abstr.*, 1917, **2**, 497—498).—If a solvent (potassium ferricyanide) is added to the copper solution in amount less than is necessary to dissolve all the cuprous oxide, the reagent will remain clear until all the cyanide has combined with the greater part of the oxide; then a bulky precipitate occurs, and this sign of the end of the reaction is easily recognised. G. B.

A Rapid Method for the Estimation of Sugar in Urine. OTTO MAYER (*Münch. med. Woch.*, 1917, **64**, 1222—1223; from *Chem. Zentr.*, 1917, **2**, 653—654).—A mixture of 10 c.c. of the urine with 10 c.c. of 15% sodium hydroxide solution is diluted to 50 c.c. with water, and a $2\cdot5\%$ solution of copper sulphate gradually added, with shaking, until the precipitate has almost entirely redissolved and a just perceptible permanent turbidity remains,

which increases somewhat on keeping. Under these conditions, each c.c. of the copper sulphate is equivalent to 0·1% of dextrose. If the urine contains more than 4% of dextrose, only 5 c.c. should be used, whilst if less than 0·5—1% is present, 20 c.c. should be taken. Should the urine give a precipitate of calcium phosphate, it should be previously treated with a measured proportion of sodium hydroxide solution, and a suitable fraction of the filtrate submitted to the above titration. Very turbid urines should be filtered, and excessive quantities of albumin removed by boiling before a sample is submitted to the above analytical process.

D. F. T.

Acidosis. VII. Estimation of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Urine. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1917, **32**, 455—493).—Dextrose and other interfering substances are first removed by treating 25 c.c. of the urine in a 250 c.c. measuring flask with 100 c.c. of water, 50 c.c. of a 20% copper sulphate solution, and, after mixing, 50 c.c. of 10% suspension of calcium hydroxide in water. After shaking and testing with litmus (if not alkaline, more calcium hydroxide is added), the mixture is diluted to the mark and allowed to remain for at least one-half hour for dextrose to precipitate. It is then filtered through a dry filter paper.

To estimate the total acetone substances, 25 c.c. of the urinary filtrate are placed in a 500 c.c. flask and boiled with 100 c.c. of water, 10 c.c. of 50% sulphuric acid, and 35 c.c. of 10% mercuric sulphate (73 grams of pure red mercuric oxide dissolved in 1 litre of 4N-sulphuric acid) under a reflux condenser. After boiling has begun, 5 c.c. of a 5% solution of potassium dichromate are added, and the boiling continued for one and a-half hours. The yellow precipitate which forms consists of an acetone–mercury–sulphate–chromate compound, and it is collected on a tared Gooch crucible, washed with 200 c.c. of cold water, and dried for an hour at 110°. After cooling in the air, it is weighed, or the precipitate may be dissolved in hydrochloric acid and titrated with standard potassium iodide solution.

The acetone plus the acetoacetic acid is estimated exactly as the total acetone substances, except that (1) no dichromate is added, and (2) the boiling is continued for not less than thirty and not more than forty-five minutes. The hydroxybutyric acid may be estimated separately by first acidifying with sulphuric acid and boiling off the acetone and acetoacetic acid. The factors for calculating the results are 1 mg. acetone yields 20 mg. of precipitate and 1 mg. hydroxybutyric acid yields 8·45 mg. of precipitate. In acetonuria, hydroxybutyric acid usually represents 75% of the total acetone substances.   H. W. B.

Acidosis. VIII. Estimation of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Blood. DONALD D. VAN SLYKE and REGINALD FITZ (*J. Biol. Chem.*, 1917, **32**, 495—497. Compare preceding abstract).—The proteins are first removed by

precipitation with mercuric sulphate, and the acetone substances are then estimated in the resulting filtrate exactly as described for urine (*loc. cit.*). H. W. B.

A Biological Colour Reaction for Succinic Acid. T. THUNBERG (*Svenska Läkareförenigenshandlingar*, 1917, **43**, 996—1001; from *Physiol. Abstr.*, 1918, **2**, 655. Compare this vol., i, 140).—The amount of succinic acid in tissues may be estimated as follows. The organ is extracted with amyl alcohol, and this is then extracted with ether. The ethereal extract is neutralised and its decolorisation effect in a solution containing methylene-blue and muscle is observed. By this means, 0·02 mg. of succinic acid can be detected and estimated. W. G.

The Test for Tartrates Depending on the Formation of the Copper Tartrate Complex. L. J. CURTMAN, A. LEWIS, and B. R. HARRIS (*J. Amer. Chem. Soc.*, 1917, **39**, 2623—2630).—The test for tartrates, which depends on the solubility of cupric hydroxide in alkaline solutions of the alkali tartrates, has been submitted to examination with the object of determining its sensitiveness. By the use of potassium ferrocyanide instead of ammonia for the detection of the dissolved copper in the filtered solution, it has been found possible to detect 0·2 mg. of tartrate.

Solutions which contain ammonium salts, arsenites, borates, or phosphates give a positive reaction in the absence of tartrates. Chromates, ferrocyanides, and ferricyanides interfere by masking the test colour, whilst cyanides readily dissolve cupric hydroxide. One mg. of tartrate gives a negative result in the presence of 500 mg. of thiosulphate, arsenate, chromate, fluoride, thiocyanate, nitrite, or acetate and also in the presence of 250 mg. of thiosulphate, oxalate, thiocyanate, or nitrite. Many organic substances interfere with the application of the test. H. M. D.

Comparison between the Bromide–Bromate Method and the Methods of Hübl and of Wys for the Estimation of the Iodine Number of Oils and Fats. C. KELBER and H. RHEINHEIMER (*Arch. Pharm.*, 1917, **255**, 417—424).—All three methods give concordant results for oils and fats having small iodine numbers, including hydrogenised oils which before hardening had large iodine numbers but have been extensively saturated by the addition of the hydrogen. The bromide–bromate method always gives too low results in the case of oils having large iodine numbers. The authors prefer the method of Wys to that of Hübl.

C. S.

A Method for the Estimation of Uric Acid in Small Quantities of Blood, Urine, and other Body Fluids. A. KOWARSKY (*Berlin Klin. Woch.*, 1917, **54**, 987—989; from *Physiol. Abstr.*, 1918, **2**, 586).—Proteins are first completely precipitated and removed, and the filtrate is concentrated to 2 c.c. The uric

acid is precipitated by ammonium chloride, and the ammonia in the precipitate estimated by the formalin method. Accurate results are reported.   W. G.

Estimation of Phytin Phosphorus in Plant Products. J. B. RATHER (*J. Amer. Chem. Soc.*, 1917, **39**, 2506—2515).—The ferric chloride titration method described by Heubner and Stadler (A., 1914, ii, 690) may be applied to the estimation of phytin in vegetable substances. Maximum extraction of the phytin phosphorus is attained by extraction with 1·2% hydrochloric acid for three hours. Non-phosphorised substances and phosphorus compounds other than phytin do not interfere with the estimation. The largest amount of phytin phosphorus was found in wheat bran, rice bran, rice polish, and cotton-seed meal (0·76 to 1·26%), and the smallest in maize, oats, soja beans, and clover seed (0·19 to 0·36%). [See, further, *J. Soc. Chem. Ind.*, 1918, 17A.]
W. P. S.

The Simplest and most Convenient Method for the Detection of Albumin in Urine. F. LENZ (*Münch. Med. Woch.*, 1917, **64**, 1267; from *Physiol. Abstr.*, 1918, **2**, 613).—In this method only one reagent, namely, sulphosalicylic acid, is used, and heat is not necessary.   W. G.

Colorimetric Estimation of Hæmoglobin. WALTER W. PALMER (*J. Biol. Chem.*, 1918, **33**, 119—126).—The blood is obtained in the usual manner, by pricking the finger or lobe of the ear. It is diluted by drawing 0·05 c.c. into a special pipette and transferring into 5 c.c. of 0·4% ammonium hydroxide solution contained in a test-tube. After rinsing out the blood pipette by drawing the ammonium hydroxide solution into it two or three times, ordinary illuminating gas is bubbled rapidly through the ammonia–blood solution for thirty seconds. It is then compared in a Duboscq colorimeter with a standard carbon monoxide hæmoglobin solution set at 10. For the preparation of the standard solution, a quantity of human or ox blood is obtained, and its oxygen capacity estimated (compare Van Slyke, this vol., ii, 82). The blood is diluted with 0·4% ammonium hydroxide solution, so as to make a 2% solution of a blood with an oxygen capacity of 18·5%, and it is then saturated with carbon monoxide. This stock solution will keep for many months, and the standard solution can be prepared from it at any time by diluting 5 c.c. to 100 c.c. with 0·4% ammonium hydroxide solution. The accuracy of the estimation is usually within 1%. [See also *J. Soc. Chem. Ind.*, 1918, March.]   H. W. B.

General and Physical Chemistry.

Drude's Theory of Dispersion from the Point of View of Bohr's Model and the Constitution of H_2, O_2, and N_2.
A. SOMMERFELD (*Ann. Physik*, 1917, [iv], **53**, 497—550).—A theoretical paper in which the author discusses the question of the dispersion and magnetic rotation of gases on the assumption that the structure of the molecules is in accordance with Bohr's hypotheses. The theoretical considerations are applied to hydrogen, oxygen, and nitrogen, for which certain structures are assumed, and the calculated refractive, dispersive, and magnetic rotatory powers are compared with those found by experiment. H. M. D.

The Spectra of Isotopes and the Vibration of Electrons in the Atom. WILLIAM D. HARKINS and LESTER ARONBERG (*Proc. Nat. Acad. Sci.*, 1917, **3**, 710—714).—The wave-length of the line $\lambda 4058$ in the spectra of ordinary lead and of lead from radium (radium-G) has been measured with great accuracy by the use of a 10-in. plane grating, giving a sixth order spectrum with a dispersion of 0·359 Å. per mm. The atomic weight of the specimen of radium-G employed had been found by Richards to be 206·34, compared with 207·18 for ordinary lead.

In order to avoid mechanical shifts, the two spectra were photographed simultaneously, the vacuum arc lamps employed as sources of light being interchanged from time to time during the taking of the records. In all, seventeen experiments were made, and the plates show in all cases that the wave-length of the line $\lambda 4058$ in the spectrum of radium-G is greater than it is in ordinary lead, the average difference being equal to 0·0043 Å

The observations are said to establish definitely the existence of a measurable difference between the wave-lengths of corresponding lines in the spectra of isotopes. The photographs indicate clearly that the shift is real and cannot be explained by broadening. H. M. D.

Arc Spectrum of Gadolinium. JOSEF MARIA EDER. (A communication from *Photochem. Lab. d. K. K. Graph. Lehr-u. Versuchsanstalt Wien*, 1467—1535; from *Chem. Zentr.*, 1917, ii, 362).—The author has investigated this spectrum with the aid of gadolinium products obtained by Auer by a fractionation which separated gadolinium from samarium and europium. The chloride gives a purer spectrum than the oxide. The tables of gadolinium lines measured occupy 62 quarto pages. The fractions containing europium prepared by Auer give indications spectroscopically of the presence of an unknown element lying between europium and samarium. R. V. S.

The Spectrum of Nickel. J. E. PAULSON (*Physikal. Zeitsch.* 1918, **19**, 13—15).—An examination of the wave-lengths of lines,

In cross references to abstracts *Ind.* will be used in place of *J. Soc. Chem. Ind.*, 1918, **37**.

in the arc spectrum of nickel has shown the existence of thirty-three groups of eight lines with constant differences between the corresponding wave-numbers. The lines in question are tabulated and the relative intensities are shown.   H. M. D.

The Ultimate Rays of Great Sensitiveness of Columbium and Zirconium. A. DE GRAMONT (*Compt. rend.*, 1918, **166,** 365—368).—Under the conditions previously described for titanium (compare this vol., ii, 49), the ultimate rays of columbium which could be detected photographically were $\lambda = 4101\cdot0$, $4079\cdot7$, $4059\cdot0$. None of these was visible to the eye at dilutions much above $1 : 100$. The ultimate rays of zirconium were $\lambda = 3496\cdot2$, $3438\cdot2$, $3392\cdot0$. The sensitiveness of the group of five rays in the blue, $Zr\alpha$, was small.   W. G.

Resonance Spectra of Iodine. R. W. WOOD (*Phil. Mag.*, 1918, [vi], **35,** 236—252. Compare A., 1913, ii, 994 ; 1914, ii, 233).—An account is given of further observations on the resonance spectra which are emitted by iodine vapour when this is excited by the light from a Cooper-Hewitt mercury lamp. An improved method of illumination is described.

The doublet series, which is excited by the green mercury line, has been found to extend towards the red end of the spectrum up to $\lambda 7685$. The photographs, obtained by means of plates sensitised with dicyanine, show most of the doublets of the series, the last doublet at $\lambda 7685$ being of the twenty-seventh order. It is probable that this represents the limit of the resonance spectrum, for the plates used were highly sensitive to beyond λ 8500. The position of the twenty-seventh order doublet is, moreover, approximately the same as the limit of the absorption spectrum.

If the plates are exposed to the resonance radiation for longer periods, the doublets are found to be accompanied by faint companion lines, some of·which may be due to excitation by the satellites of the green mercury line, but the author considers that some are to be attributed to the stimulating influence of the green line itself. On greatly prolonged exposure, it is found that the doublets fuse together to form a series of wide bands. If a gas of the helium group is introduced into the iodine tube, the intensity of the doublets is greatly reduced, and a series of fluted bands makes its appearance. These bands, which occupy positions between the doublets, are not exhibited by the resonance spectrum of iodine in a vacuum. It is probable that the lines forming the doublets are themselves constituents of the fluted bands, and that the appearance of the bands in presence of an inert gas is due to a transfer of energy from one part of the vibrating system to another as a result of collisions between iodine molecules and molecules of the inert gas. It may in this way be possible to account for the complicated system of bands in the absorption spectrum, these bands being referred to simpler systems which can be excited separately.

If the iodine vapour in a vacuum is excited by means of a quartz mercury arc, complicated groups of lines are obtained in place of the doublet series. This is attributed to the circumstance that, under these conditions, the green mercury line has broadened to such an extent that it covers a number of the iodine absorption lines. The intensity distribution amongst the groups of lines produced by this multiplex excitation is approximately the same as the distribution in the doublet series. The complexity of the groups increases with the width of the green exciting line.

A short reference is made to the resonance spectra excited by the two yellow mercury lines, but these have not yet been examined in detail.   H. M. D.

Series Law of Resonance Spectra. R. W. WOOD and M. KIMURA (*Phil. Mag.*, 1918, [vi], **35**, 252—261. Compare preceding abstract).—The wave-lengths of lines in the resonance spectra of iodine are recorded and the law of distribution is discussed.

The series of strong doublets excited by the green line of the Cooper-Hewitt lamp has been examined with particular care, with the result that the frequency difference between the components is found to be constant and equal to 50. The spacing of the first member (shorter λ component) of each doublet is represented by the formula $1/\lambda_m = 183075 - 2131\cdot414 + 12\cdot734m(m-1)/2$, in which λ_m is the wave-length of the first member of the doublet of the mth order. The agreement between the calculated and observed values is quite good up to the doublet of the fifteenth order, but as the order becomes greater the divergence increases.

Other series of doublets with constant frequency differences may be approximately represented by a similar formula.

The lines in the resonance spectrum excited by the yellow lines $\lambda\,5769\cdot6$ and $\lambda\,5790\cdot7$ have also been examined with reference to the law of distribution. The doublets in these groups of lines are not characterised by the same regularities as those in the groups excited by the green mercury line. The frequency difference between the components has not a constant value, but the spacing of the doublets in the groups of lines excited by the yellow line $\lambda\,5769\cdot6$ is such that the difference between the successive values of $1/\lambda$ is nearly constant. The degree of constancy is not so pronounced for the case of the groups which are excited by $\lambda\,5790\cdot7$.   H. M. D.

Absorption Spectrum of Oxyhæmoglobin in the Ultraviolet and Extreme Ultra-violet Regions. TOSHIKAZU MASHIMO (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 199—202).—Oxyhæmoglobin, purified by crystallisation, was dissolved in water and the photographic records obtained by interposing layers of this solution, varying in thickness in the ratio of the integral numbers from 1 to 42, between a carbon arc and the photographic plate, are compared. These records show an absorption band with the centre at $\lambda\,350\,\mu\mu$, which is possibly the same as that described by Peyrega

and Vlès as occurring at λ 333 μμ (*Compt. rend.*, 1912, **154**, 133). No absorption could be detected in the Schumann region.

<div align="right">H. M. D.</div>

The Fluorescence of Cyano-compounds. HUGO KAUFFMANN (*Ber.*, 1917, **50**, 1614—1623).—See this vol., i, 113.

Rotation Inversion and Anomalous Rotation Dispersion. HERMANN GROSSMANN and MARIE WRESCHNER (*J. pr. Chem.*, 1917, [ii], **96**, 125—165).—The dextrorotatory power of tartaric acid in aqueous solution is probably due to the dissociation of the acid, because with increasing concentration of the solutions the rotation falls, and, indeed, the molten or solid acid is lævorotatory. Addition of acids such as hydrochloric or nitric acid to the aqueous solution depresses the dissociation, the normal rotatory dispersion curve which rises from red to violet becoming gradually altered by an increasing proportion of added acid until a falling curve results; during the inversion of the nature of the curve the latter exhibits a maximum, which gradually moves in the direction of increased wave-length as the concentration of added acid is raised. Acetic acid exerts a similar effect to hydrochloric and nitric acids, but is less powerful. Sulphuric acid at low concentrations gives an effect resembling that of nitric and hydrochloric acids, but at higher concentrations the curve again begins to rise, and, in pure sulphuric acid, tartaric acid shows rotation values [α] red +69 and [α] violet +158·8, which are above those observed with any other solvent. With boric acid the rotatory dispersion curve of tartaric acid is unaffected in type, probably because of the formation of complex compounds of the two acids (compare Grossmann and Wieneke, A., 1906, ii, 209).

On adding increasing quantities of sodium hydroxide to the dextrorotatory aqueous solution of sodium tartrate, the rising rotatory-dispersion curve gradually flattens, and then, after becoming coincident with the horizontal axis corresponding with zero rotation, finally falls below on to the negative side of this axis; this alteration is attributed to the reversible formation of a lævorotatory tetrabasic salt of the acid. The addition of a calcium, strontium, magnesium, or cerium salt to the solution of tartaric acid containing excess of sodium hydroxide causes the curve for the alkaline solution to alter its character and to become wholly positive, doubtless due to the formation of complex compounds; a zinc salt gives no such evidence of complex formation.

Malic acid in the pure condition is dextrorotatory, but in the ionised condition exhibits a lævorotation; the addition of acids to the aqueous solution, as with tartaric acid, tends to repress dissociation, and the rotatory dispersion curve for the solution, which normally falls as it passes from red to violet, rapidly changes into a rising positive curve with the addition of increasing quantities of acid. Again, sulphuric acid at low concentration behaves like the other aqueous mineral acids, but in pure sulphuric acid malic acid attains the extreme negative values [α] red −27°, [α] violet −60·4°.

The effect of excessive sodium hydroxide on the activity of sodium malate solution resembles that with aqueous sodium tartrate; the rotatory dispersion curve becomes gradually flattened, and finally passes over to the other side of the horizontal axis representing zero-activity, the transition in this case being upwards from the negative side to the positive.

So-called anomalous rotatory dispersion as evidenced by maximum and minimum values or by achromatism occurs only in the neighbourhood of zero rotation, and the evidence indicates that it is due to the presence of two optically active components of different optical activity. Lowry's suggestion (A., 1914, ii, 786), to use the terms " simple " and " complex " rotatory dispersion in place of " normal " and " anomalous," is commended.   D. F. T.

The Relation of Position Isomerism to Optical Activity. XI. The Menthyl Alkyl Esters of Terephthalic Acid and its Nitro-derivatives. JULIUS BEREND COHEN and HANNAH SMITH DE PENNINGTON (T., 1918, **113**, 57—66. Compare A., 1916, ii, 206).—The average molecular rotation of seven menthyl alkyl esters of terephthalic acid is found to be $[M]_D^{20}$ $-254°$, and the rotation of menthyl hydrogen terephthalate to be $[M]_D^{18}$ $-259·2°$, which may be compared with $-239°$ for menthyl benzoate, $-243°$ for menthyl alkyl phthalates, and $-332°$ for menthyl hydrogen phthalate. It appears, therefore, that the carbalkoxyl or carboxyl group has little influence, in the para-position, on the activity of the asymmetric carbon atom. In the case of some menthyl alkyl nitroterephthalates, it is likewise found that enhanced rotation is exhibited by those esters in which the nitro-group is adjacent to the active group. A strange abnormality is met with among these particular o-nitro-esters; the solutions in benzene have considerably higher rotations than the fused esters.

For details of the preparation and constants of these esters, see the original.   J. C. W.

Absorption of Hard Röntgen Rays in Gases. MINNA LANG (*Ann. Physik*, 1917, [iv], **53**, 279—319).—The experiments described were made with highly penetrating rays, the absorptive powers of oxygen, nitrogen, air, carbon dioxide, hydrogen, sulphur dioxide, and methyl chloride being compared. The results obtained show the relative values of the absorption-coefficients for rays of varying penetrating power and the dependence of the absorptive power on the pressure of the gas. A comparison is made of the absorptive capacity of air for Röntgen rays and γ-rays. H. M. D.

Interpretation of Röntgen Spectra. L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 328—343).—A theoretical paper, in which the author discusses the origin of the several series of lines which have been recognised in the high frequency spectra. It is assumed that the atoms are built up in accordance with Bohr's theory, and that the high frequency emission is to be explained on the lines adopted by this author.

According to Debye (A., 1917, ii, 434), the emission of the K series of lines is due to an inner ring of three electrons. This appears to be the most probable cause of the appearance of these lines, but it is shown that changes in a four-ring system of electrons may also account for the series.

The L and M series require the assumption of rings of electrons, the disturbance of which is associated with two or more energy quanta, and it is suggested that the origin of the L series is a seven-membered ring of electrons corresponding with two energy quanta, the l series an eight-membered ring with two quanta, and that the M series is due to a ring of nine electrons associated with three energy quanta.   H. M. D.

Atomic Structure on the Basis of Röntgen Spectra.

L. VEGARD (*Ber. Deut. physikal. Ges.*, 1917, **19**, 344—353).—The theoretical considerations advanced in explanation of the origin of the K, L, l, and M series of high frequency lines (compare previous abstract) have led the author to devise models for the structure of the known elements. It is claimed that this system of models is in agreement with the periodicity in the properties of the elements. With increasing atomic number there is a gradual increase in the number of concentric electron rings, but each ring appears to retain its individual characteristics throughout the entire series of elements. Such characteristics are the number of the constituent electrons and the energy quanta with which these are associated. The number of quanta increases, in general, with the diameter of the ring.   H. M. D.

Resonance and Ionisation Potentials for Electrons in Cadmium, Zinc, and Potassium Vapours.

JOHN T. TATE and PAUL D. FOOTE (*Proc. Nat. Acad. Sci.*, 1918, **4**, 9).—According to the observations of Franck and Hertz, there are certain definite potentials at which electrons cause the emission of rays by the atoms of a gas or vapour. Two types of collision occur, one of which is accompanied by the emission of a single frequency, whilst the other causes ionisation and gives rise to a composite spectrum. The corresponding potentials are distinguished as resonance and ionisation potentials, and these critical values of the potential have been determined for cadmium, zinc, and potassium vapours.

Within the limits of experimental error, the observed critical potentials agree with the values calculated from the quantum relation $h\nu = eV$, in which ν is the frequency of the single line in the case of the resonance radiation and the limiting frequency of the line series when the radiation is due to ionisation.   H. M. D.

Nomenclature of the Radio-elements.

ST. MEYER and E. VON SCHWEIDLER (*Zeitsch. Elektrochem.*, 1918, **24**, 36—38; *Physikal. Zeitsch.*, 1918, **19**, 30—32).—The authors, in a work published on radioactivity, have made a number of changes in the symbolic representation of radioactive substances. The changes, which have been assented to by twenty-nine German and Austrian chemists and physicists, consist chiefly in the following: (1) Isotopes are desig-

nated by Roman indices, for example, U_I, U_{II}. (2) Successive dis-integration products are designated by Arabic indices, for example, UX_1, UX_2. (3) Branched products are designated by dashes, for example, RaC', RaC'', the single dash indicating that the substances are like polonium and the double dash those like thallium.

J. F. S.

The Colloidal State of Radioactive Substances. HILARY ZACHS (*Kolloid Zeitsch.*, 1917, **21**, 165—176).—Many recorded observations show that certain radioactive substances in neutral or slightly alkaline solution exhibit properties which are usually regarded as characteristic of colloids, although the concentration of the solution is very much smaller than that corresponding with saturation with respect to the hydroxide. It has been suggested that the behaviour of these radioactive solutions is due to the presence of colloidal impurities in the solution, but certain facts cannot be reconciled with this hypothesis.

In the attempt to obtain further information on the subject, the author has investigated the properties of radium-A, radium-B, and radium-C in various solvents, including water, ethyl alcohol, ethyl ether, ethyl malonate, and benzene. The nature of the solvent is of considerable influence on the behaviour of the solutions in an electric field. In the case of water solutions, for instance, radium-A is deposited on the anode, radium-B on the cathode, and radium-C to a small extent on the anode, whereas in alcoholic solution, radium-A is deposited on the cathode and radium-B and -C on the anode. The sign of the change of the colloidal particles does not depend entirely on the nature of the solvent, for in every case, particles of opposite sign appear to be present. The results obtained with alcoholic solutions show, moreover, that the relative amounts of substance deposited on the two electrodes vary with the applied potential. This effect has been previously noted in the case of colloidal solutions of silver.

The adsorption of the radioactive colloids by various adsorbents is also found to exhibit a similar variation when the solvent is changed. The variability is said to afford evidence of the presence of particles of different degrees of dispersity, and it is suggested that the radioactive substances occur in the form of ions as well as in colloidal form.

Although cellulose has but little adsorptive capacity for the radioactive substances, it is found that comparatively large quantities of the radioactive products remain on the filter when the above solutions are passed through an ordinary filter paper. This would seem to show that a considerable proportion of the radioactive dispersoid particles are of large dimensions, and the suggestion is made that these particles contain a very large number of solvent molecules.

The decay of radium emanation in a gas or vapour leads apparently to the formation of gaseous ions by the combination of the particles of radium-A, -B, and -C with the molecules of the gas or

vapour present. This type of combination or condensation seems to be very different in kind, however, from that which occurs in liquid solvents, in which, apparently, the degree of solvatation is such that colloidal properties are developed.   H. M. D.

Radioactive Minerals in Bavaria. II. F. HENRICH (*J. pr. Chem.*, 1917, [ii], **96**, 73—85).—The view that the fluorspar (so-called "Stinkfluss") of Wölsenberg, near Wölsendorf, in the Upper Palatinate, owes its colour and odour to radioactive influences has been experimentally tested.

Crystallised colourless fluorspar can be coloured deep blue by the β- and γ-rays of radium, and then shows on gentle warming a beautiful green thermoluminescence, which fades and changes into the pale violet light characteristic of all fluorspars. But neither by radium nor by positive rays (Kanalstrahlen) could the characteristic odour of Wölsenberg fluorspar be produced. According to O. Ruff, this odour, which is produced when the mineral is crushed, is typical of free fluorine, and indeed the mineral may be used to demonstrate conveniently the odour of this difficultly prepared element.

The second part of the paper deals with the detailed analysis of copper–uranium mica (chalcolite or tobernite) from Steinbruch Fuchsbau, near Leopoldsdorf, in the Fichtelgebirge, the composition of which agreed closely with the formula

$$Cu(UO_2)_2(PO_4)_2,11 \cdot 5H_2O.$$

F. S.

The Radioactivity of Archæan Rocks from the Mysore State, South India. W. F. SMEETH and H. E. WATSON (*Phil. Mag.*, 1918, [vi], **35**, 206—214).—Some fifty radium estimations have been made of representative samples from the various components of the Archæan complex of Mysore, in order to see how far the various formations or groups are distinguishable by their radioactivity. These are set forth in order of age of the rock in a table. The oldest, the hornblende rocks (epidiorites and hornblende schists) of the Dharwar system, are low in radium and uniform, between 0·14 and 0·25 ($\times 10^{-12}$ gram of radium per gram of rock), and the rocks of the chloritic series, next in age, do not differ much from them. Intrusions of the Champion gneiss and the related quartz veins of the Kolar Field, which contain much more radium than the normal schists, considerably increase the radium content, whereas the basic intrusions of Dharwar age contain much less radium than the schists themselves. On radioactive evidence, the original classification which correlated the Bellara trap with the Grey trap of Chitaldrug is correct, rather than the newer correlation of the latter with the Santaveri trap of the Kadur district, which resembles it closely, but contains three times as much radium as the other two. This affords an example of the possible use of such determinations in the correlation of the highly metamorphosed members of the Archæan complex.

The Champion gneiss, Peninsular gneiss, and Closepet granite, next in age, contain four to five times as much radium as the Dharwar schists and twelve to fifteen times as much as the next and following Charnockites, which stand apart from the others in virtue of exceedingly low radium content. This confirms Holland's classification of Charnockites as a distinct petrographical province.

The general conclusions are that these very ancient rocks, all supposed to be of igneous origin, contain remarkably little radium. For the fairly uniform hornblendic schists of the Kolar Field, the radium content does not vary with the depth from the surface. Amongst magmas, the more basic contain less radium than the more acid, the Charnockite magma of intermediate composition being a striking exception. F. S.

Influence of Heat Treatment on the Electrical and Thermal Resistivity and Thermo-electric Potential of some Steels. EDWARD D. CAMPBELL and WILLIAM C. DOWD (*J. Iron Steel Inst.*, 1917, **96**, 251—266).—In a series of annealed and hardened steels containing from 0·018 to 1·184% of carbon, the ratio of the electrical resistivity to the relative thermal resistivity is in all cases higher than for pure iron. The effect of quenching is to raise both values. The thermo-electric potential varies with the nature as well as with the concentration of the elements dissolved in the iron. [See, further, *Ind.*, 1917, 1051.] C. H. D.

A Permanganate Electric Cell. A. W. WARRINGTON (*Chem. News*, 1918, **117**, 97—98).—Potassium permanganate is used as the depolarising agent in a two-fluid electric cell, in which the carbon plate is immersed in a dilute solution containing 3·16 grams of potassium permanganate and 6 c.c. of concentrated sulphuric acid in 250 c.c. of liquid, contained in a porous pot. The outer zinc compartment, of 750 c.c. capacity, contains a strong solution of zinc sulphate (14·55 grams). The cell gave a voltage of about 2. Two such cells were connected up to a water voltameter and tangent galvanometer in series, and, after the first ten minutes, the fall in current in a run extending over three hours forty-six minutes was from 0·09 to 0·085 ampere only, and the voltage at the end was still 3·7. With a single-fluid permanganate cell containing the same amounts of permanganate and sulphuric acid with amalgamated zinc and carbon, the current, after ten minutes, fell from 0·0538 to 0·0358 ampere in 146 minutes, whilst the voltage at the end was 1·5. The yield of current with very dilute solutions in a two-fluid cell is very high, and a cell containing 0·79 gram of potassium permanganate and 2·64 grams of sulphuric acid in 250 c.c. of liquid, and 3·59 grams of crystallised zinc sulphate in 750 c.c., deposited 0·48 gram of copper in three hours, whilst nearly 75% of the energy was still available. A similar dichromate cell, containing 5·88 grams of potassium dichromate and 13·72 grams of concentrated sulphuric acid in the carbon compartment, gave an average current of 0·0632 ampere only. B. N.

The Magnetic Properties of Manganese and of some Manganese Steels. SIR ROBERT HADFIELD, C. CHÉNEVEAU, and CH. GÉNEAU (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 65—87; *Compt. rend.*, 1918, **166**, 390—392).—Measurements have been made of the coefficient of magnetisation of manganese, free from occluded gases, and a number of manganese steels. Manganese is paramagnetic. [For numerical data, see *Ind.*, 12A.]   W. G.

Energy Theory of Matter. ELMER B. VLIET (*Chem. News*, 1918, **117**, 118—119).—It has been pointed out by Thornton (A., 1917, ii, 164) that the molecular heat of combustion of an organic compound is proportional to the number of oxygen atoms which is required for the complete combustion of one molecule of the organic substance. According to Redgrove (A., 1917, ii, 411), the molecular heat of combustion can be represented by an additive series of terms which depend on the number and type of the valency bonds in the molecule.

By applying these relations to the aliphatic hydrocarbons, it is shown that the coefficients characteristic of the several terms in Redgrove's series may be calculated. The values so obtained differ from those calculated by Redgrove, and the conclusion is drawn that the molecular heat of combustion cannot be regarded primarily as a function of the number and type of the valency bonds. It is, however, still possible that the energy change accompanying a reaction may depend on the valency changes.

H. M. D.

A High Temperature Thermostat. J. L. HAUGHTON and D. HANSON (*J. Inst. Metals*, 1917, **18**, 173—186).—The instrument consists in principle of a double-walled vessel, like a Bunsen ice calorimeter, made into a furnace by winding with nichrome wire. The vessel acts as a gas thermometer, and the variations of pressure of the air contained in it operate a contact-breaker, consisting of a U-tube containing mercury with two platinum contacts, through which passes a relatively small current. The latter, by means of a solenoid, pulls a fork out of or into two mercury cups, so introducing an external resistance into the heating circuit or cutting it out. The other side of the U-tube is connected with a second thermostat of simpler construction, which serves to compensate for changes of external pressure and temperature.

The furnace bulb is made of silica, and may be used for temperatures of the order of 1000°. The U-tube has a tap for removing the mercury when fouled by sparking, and is made sufficiently wide in the upper part of the limbs to prevent the mercury from being sucked back when the furnace is shut off. The cold thermostat consists of three concentric cylinders, of which the inner one acts as the air-bulb, and is surrounded by benzene contained in the middle vessel, on which a fine resistance wire is wound. The benzene, in expanding, operates a mercury contact-breaker. The third cylinder contains insulating material. With this arrange-

ment, the temperature of this part of the apparatus is constant within less than 0·1°. The main furnace is then kept constant within 1°.

By connecting another furnace, such as a crucible furnace, in series with the main regulating resistance, but in parallel with a thermostat furnace, the temperature of the former may be kept constant with about the same accuracy as the thermostat. By automatically reducing a resistance in parallel with the controlled furnace, very regular cooling may be obtained, such as is required in taking cooling curves.   C. H. D.

Adsorption Compounds and Adsorption. III. The Influence of the Adsorption of certain Substances by Alcohol. L. BERCZELLER and ST. HETÉNYI (*Biochem. Zeitsch.*, 1917, **84**, 137—148).—A number of measurements are given of the adsorption of alkali hydroxides, acetic acid, iodine, methylene-blue, etc., by starch, charcoal, etc., and the influence of the additions of alcohols. The influences of isocapillary and equimolecular solutions of the alcohols on adsorption were compared. Generally, the isocapillary solutions did not exert the same amount of inhibition, the solutions of lower alcohols, which contain a relatively large amount of alcohol, exerting a greater inhibition than isocapillary solutions of the higher alcohols. Those isomolecular solutions of which the surface tensions are lowest exert, however, a greater inhibitory action.   S. B. S.

Gliding Dialysis. II. H. THOMS (*Ber.*, 1918, **51**, 42—45. Compare A., 1917, ii, 561).—Instead of rotating the dialyser about the plane of the membrane, it may be rotated or shaken in the same plane, with equally good results. The new arrangement is an improvement, inasmuch as it imposes very little tearing strain on the membrane. [See, further, *Ind.*, 190A.]   J. C. W.

Solubility and Dissociation of some Electrolytes in Ethylurethane. M. STUCKGOLD (*J. Chim. Phys.*, 1917, **15**, 502—516).—The author has determined the solubilities of the following salts in ethylurethane at 60°: ammonium, rubidium, potassium, tetramethylammonium and tetraethylammonium iodides, sodium, potassium, rubidium, and tetramethylammonium bromides, sodium, potassium, and ammonium chlorides. The conductivities of six electrolytes, namely, ammonium, potassium, and tetraethylammonium iodides, tetramethylammonium bromide, cobalt nitrate, and zinc nitrate, have been determined, those of the iodides being taken to the greatest dilutions suitable, considering experimental errors. The cryoscopic constant of this solvent, using naphthalene, carbamide, and nitrotoluene as solutes, was found to be 53·2, and from this, molecular weight determinations by the cryoscopic method indicated that ammonium, potassium, and rubidium iodides are dissociated in ethyl urethane.

Molecular weight determinations on ethylurethane, based on the

capillarity constant, using the formula $M = 0.6T(4.8 - \log p)/a_2$, where T is the absolute b. p. at p mm. of mercury and $a_2 = h . r$, where h is the height of ascension and r the radius of the capillary in millimetres, show that ethylurethane is strongly polymerised, the factor of association being almost independent of the temperature over the range 65—179°. The viscosities and densities of the urethane at 60°, 70°, and 80° were also determined.   W. G.

Ultrafiltration of Supersaturated Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 156—159).—Supersaturated solutions of menthol, thymol, and naphthol were filtered through collodion membranes, and the surface tensions of filtrate and residue were determined by the stalagmometer. In certain cases, the results (lower surface tension of residue) indicated that some of the solute was retained on the filter, from which fact the conclusion is drawn that the supersaturated solution is colloidal in character.

S. B. S.

Colloidal Nature of the γ-Alkali Resin Soaps. LUDWIG PAUL (*Kolloid Zeitsch.*, 1917, **21**, 176—191).—A general account is given of the properties of solutions of sodium and ammonia resin soaps in which particular attention is directed to the colloidal properties of the solutions and to differences between the resin and fatty acid soaps. Dilute solutions of the alkali resin soaps represent highly disperse colloid systems of very pronounced stability. On the addition of basic dyes, such as methyl-violet and magenta, colloidal lakes are formed which can be kept without change for prolonged periods of time. The lakes are coagulated on the addition of suitable electrolytes.

On addition of hydrochloric acid to the γ-alkali resin soaps, γ-pinic acid is obtained, and this behaves very similarly to the soaps towards basic dyes. [See *Ind.*, April.]   H. M. D.

Colour and Degree of Dispersity [of Colloidal Solutions]. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 156—174).—Gold sols have varying colours, according to the size of the colloidal particles, and Harrison (A., 1912, ii, 240) has directed attention to the similarity of the colours of the adsorption complexes of iodine with starch and dextrins, where similar variations of colour are produced by varying the size of the particles of the carbohydrate. The author shows that similar variations in the colour of the adsorption complexes of lanthanum hydroxide can be produced by varying the size of the particles of the hydroxide. Attention is also directed to analogies in the colour variations in certain complex copper compounds, in certain reactions of bile pigments, in some furfuraldehyde reactions (Udránszky, A., 1889, 1024; 1891, 350), and in the nuances of solutions of dyes when subjected to varying treatments (heating, dilution, treatment with salts, etc.).

S. B. S.

Anisotropic Colloidal Solutions. W. REINDERS (*Kolloid Zeitsch.*, 1917, **21**, 161—165. Compare Diesselhorst and Freundlich, A., 1916, ii, 65; Kruyt, *ibid.*, ii, 486).—With a view to the explanation of the double refraction which is exhibited by certain colloidal solutions, further experiments have been made with vanadium pentoxide sols which seem to show that the particles of such sols are crystalline. By varying the conditions of formation of the pentoxide, it has been found that there is no clear line of demarcation between the particles which are present in the initially isotropic sols and those which can be microscopically identified as crystalline particles. Although the double refracting power of a sol is only developed very slowly at the ordinary temperature, the transformation takes place much more quickly at 100°. In the freshly prepared sols, the ultra-microns are spherical, but on heating at 100°, elongated ultra-microns make their appearance in a short time. These increase in size and number, and the change is accompanied by a considerable increase in the viscosity.

Experiments made with mercurous chloride and lead iodide gave similar results. If these substances are prepared by double decomposition in presence of a protective colloid, doubly refracting sols are obtained, but there is a continuous transition from the sol condition to that which is represented by crystalline suspensions of these substances.

The anisotropic character of the sols in question appears therefore to be due to the crystalline nature of the ultra-microns.

H. M. D.

Kinetics of the Reactions in the Formation and Flocculation of Colloidal Solutions. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 175—182).—Iodic acid accelerates the reduction of gold chloride solutions by sulphurous acid, as do also mercuric salts, and the colour of the sols varies in the latter case with the salt used. Examples are given of the influence of capillary active substances (hexoic and decoic acids) on the flocculation of colloidal gold and starch solutions, which are cases of sensitisation of colloids to salt precipitation, as recently demonstrated by Freundlich and Rona (A., 1917, ii, 365). S. B. S.

Coagulation and the Attraction of Particles. RICHARD ZSIGMONDY (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 1—43; from *Chem. Zentr.*, 1917, ii, 350—351 *).—The paper deals with the possibility of determining the attraction (if any) between discharged colloidal particles from measurements of the rate of coagulation. Experiments in which the changes of colour of gold hydrosols were employed as an indicator of the progress of the coagulation showed that a pure colloidal gold solution of a given nature and concentration has a certain minimum time of coagulation, independent of the nature, and to a great extent independent of the concentration, of the electrolyte employed. The period of rapid coagulation is reached before the particles are completely discharged, but the

* and *Zeitsch. physikal. Chem.*, 1918, **92**, 600—639.

remaining charges are small (compare Hardy and Powis, *Zeitsch. physikal. Chem.*, 1915, **89**, 179). The time of coagulation is approximately proportional to the gold concentration. A method of observing the progress of coagulation ultramicroscopically is given, and by this means the diminution in the number of primary particles and the production of secondary particles (which shine more brightly) were determined. From these results, it is calculated that the sphere of attraction of a primary particle is two or three times its radius. This is in agreement with the results obtained by other writers in other ways. It is proved, therefore, that the discharged particles do attract one another when they come within this distance of each other. R. V. S.

Retardation of the Formation of Prussian Blue and other Reactions in Aluminium Hydroxide Sols. JOSEF REITSTÖTTER (*Kolloid Zeitsch.*, 1917, **21**, 197—200).—In the course of observations on the coagulation of aluminium hydroxide sols in presence of various alkali metal salts (Gann, A., 1916, ii, 382), it was found that after coagulation by the addition of a very dilute solution of potassium ferrocyanide, the solution gave no blue coloration on the addition of ferric ions until after the lapse of a considerable interval of time. To explain this effect, it was suggested that the ferrocyanide ions are adsorbed and subsequently enveloped by the coagulate.

Further experiments show that the retardation is very much less pronounced if some other coagulating electrolyte, such as sodium citrate, is added to the sol either before or after the addition of the ferrocyanide. In these circumstances, it is more probable that the retardation of the formation of Prussian blue is to be explained by the adsorption of both the ferrocyanide and the ferric ions. If either or both are then displaced by other ions, conditions favourable to the formation of Prussian blue are obtained.

Similar retardation phenomena have been found when a little of the blue sol obtained by acidifying Congo-red is mixed with a colloidal solution of aluminium hydroxide and a drop of sodium hydrogen carbonate solution is added to the mixture. The blue sol may be replaced by benzopurpurin or rosolic acid. [See *Ind.*, 71A.] H. M. D.

General Curves for the Velocity of Complete Homogeneous Reactions between Two Substances at Constant Volume. GEORGE W. TODD (*Phil. Mag.*, 1918, [vi], **35**, 281—286). —By choosing suitable quantities to represent the concentration of the reacting substances, it is possible to plot curves showing the connexion between the rate of change and the time, which are applicable to all reactions of the same type. The mode of representation may be illustrated by reference to the bimolecular velocity equation $dx/dt = k(a-x)(b-x)$. If $X = x/a$, $K = ka$, and $p = b/a$, this equation assumes the form $dX/dt = K(1-X)(p-X)$, and on integration this gives $Kt = 1/(1-p) . \{\log p(1-X)/(p-X)\}$. The curves referred to are then obtained by plotting X against Kt for values of $p = 1\cdot5$, 2, 3, etc.

Corresponding series of curves are plotted for the termolecular reaction represented by $2A + B \longrightarrow$ for the three cases in which the initial concentration of A is equal to, greater, and less than that of B. Curves for the quadrimolecular reaction $3A + B \longrightarrow$ and $2A + 2B \longrightarrow$ are also shown.

These general curves may be applied in practice for the determination of k, of the value of X corresponding with a given time interval, or for the determination of the order of a reaction. If the order of the reaction and the initial concentration are known, it is only necessary to measure X corresponding with a certain value of t, and the curves then give Kt, and therefore k. The fraction X changed in a given time may be read off from the curves if the order of the reaction, the coefficient k, and the initial concentrations are known. To find the order of a reaction, it is necessary to know the initial concentrations and two corresponding values of X and t. The particular curve on which the two points (X, t) fit most exactly determines the order of the reaction.

H. M. D.

Relationship between the Saponification Velocity Constants of Esters. P. E. VERKADE (*Chem. Weekblad.*, 1918, **15**, 203—208).—The author finds that the ratio of the velocities of saponification of mixed anhydrides of acetic, propionic, etc., acids with different acids is always the same.   A. J. W.

Velocity of Saponification of certain Esters by Tenth-normal Potassium Hydroxide in Different Solvents at 25°. ERNEST ANDERSON and H. B. PIERCE (*J. Physical Chem.*, 1918, **22**, 44—67).—The object of these experiments was to determine whether the relative velocities of saponification of different esters are affected by the nature of the solvent and whether the relative rates of saponification of different esters containing the same alcohol (or acid) are independent of the nature of the alcohol (or acid).

The rates of saponification of twenty-three esters were measured at 25° in 90% methyl alcohol, 90% ethyl alcohol, *iso*amyl alcohol, D_{15}^{20} 0·8166, and, when possible, in water. The results obtained show that the relative values of the velocity coefficients in the different solvents vary considerably with the nature of the ester. Esters containing the same alcohol (acid) are saponified at relative rates which depend on the nature of the alcohol (acid).

H. M. D.

Hydrolysis of Triethyl Citrate and the Ethyl Hydrogen Citrates. JOH. PINNOW (*Zeitsch. Elektrochem.*, 1918, **24**, 21—36). —The hydrolysis of triethyl citrate, symmetrical and unsymmetrical diethyl hydrogen citrate, and symmetrical and unsymmetrical ethyl dihydrogen citrate by means of sodium hydroxide has been studied at a series of temperatures from 0° to 100°. The hydrolysis of the various stages is shown to take place at very different velocities between the temperatures of 8° and 50°. Each step in the hydrolysis may be separated from the others, and goes to completion as

a strictly bimolecular reaction. The side ethyl groups are the first to be removed, and in no circumstances do symmetrical diethyl hydrogen citrate or unsymmetrical ethyl dihydrogen citrate appear in recognisable quantities as products of any of the hydrolyses. These products are only obtainable by the esterification of citric acid. The preparative separation of the mono- and di-ethyl esters from one another and from citric acid can be effected by ether extraction from aqueous solution in a Partheil-Rose apparatus. The various esters were identified by measurements of their hydrogen ion concentration by means of the colorimetric process of Friedenthal, Salesky, and Salm. The temperature coefficient of the rate of hydrolysis is high for all five compounds at temperatures below 23°; in the case of the unsymmetrical diethyl ester and the monoethyl esters a minimum is shown between 23° and 30°, and a second minimum for the monoethyl esters between 45° and 60° and 38° and 45° respectively. The stepwise hydrolysis and the first minimum of the temperature coefficient are explained by the formation of additive products between the ester and the alkali, these compounds undergoing decomposition as the hydrolysis proceeds into the original compounds. The following reaction constants and temperature coefficients have been found: Hydrolysis of triethyl citrate, $k = 37\cdot8$ at $8\cdot1°$, $63\cdot7$ at $15°$, $98\cdot9$ at $23°$, $149\cdot8$ at $30°$, 253 at $40°$, and 443 at $50°$; increase of $\log k$ for $10°$ between the successive temperatures is $0\cdot328$, $0\cdot239$, $0\cdot259$, $0\cdot227$, and $0\cdot243$. Unsymmetrical diethyl hydrogen citrate, $k = 1\cdot725$ at $8\cdot1°$, $2\cdot92$ at $15°$, $4\cdot28$ at $23°$, $5\cdot14$ at $30°$, $9\cdot38$ at $40°$ $16\cdot17$ at $49°$; increase of $\log k$, $0\cdot330$, $0\cdot208$, $0\cdot114$, $0\cdot262$, and $0\cdot263$. Symmetrical diethyl hydrogen citrate, $k = 0\cdot474$ at $6\cdot7°$, $0\cdot841$ at $15°$, $1\cdot48$ at $23°$, $2\cdot27$ at $30°$, $4\cdot16$ at $40°$, and $6\cdot84$ at $50°$; increase of $\log k$, $0\cdot300$, $0\cdot306$, $0\cdot266$, $0\cdot263$, and $0\cdot216$. Symmetrical monoethyl hydrogen citrate, $k = 0\cdot0038$ at $0°$, $0\cdot0149$ at $15°$, $0\cdot0283$ at $23°$, $0\cdot0409$ at $30°$, $0\cdot0743$ at $38°$, $0\cdot1153$ at $45°$, $0\cdot245$ at $60°$, $0\cdot584$ at $75°$, and $2\cdot86$ at $100°$; increase of $\log k$, $0\cdot395$, $0\cdot349$, $0\cdot229$, $0\cdot324$, $0\cdot273$, $0\cdot218$, $0\cdot251$, and $0\cdot276$. Unsymmetrical monoethyl hydrogen citrate, $k = 0\cdot0825$ at $8°$, $0\cdot132$ at $15°$, $0\cdot238$ at $23°$, $0\cdot302$ at $30°$, $0\cdot511$ at $38°$, $0\cdot654$ at $45°$, $0\cdot080$ at $55°$, $1\cdot76$ at $65°$, and $10\cdot65$ at $100°$; increase of $\log k$, $0\cdot291$, $0\cdot320$, $0\cdot147$, $0\cdot285$, $0\cdot154$, $0\cdot217$, $0\cdot213$, and $0\cdot212$. The figures in all cases refer to the hydrolysis of a single ethyl group.   J. F. S.

Rate of Solution of Silver in Chromic Acid. R. G. VAN NAME and D. U. HILL (*Amer. J. Sci.*, 1918, [iv], **45**, 54—58).— The measurement of the rate at which silver dissolves in chromic acid solutions containing sulphuric acid has shown that the initial velocity is greater than the velocity which characterises the normal dissolution process. The anomaly indicates that the velocity depends on the physical state of the metal, and this in turn suggests that the rate of dissolution of the metal is not entirely determined by diffusion process.

Previous experiments have shown that the rates of dissolution of different metals tend to become more nearly equal as the concentra-

tion of the sulphuric acid in the solution increases. The behaviour of cadmium and silver forms an exception to this rule, in that the relative rates of dissolution diverge with increasing acid concentration.   H. M. D.

Contact Catalysis. IV. WILDER D. BANCROFT (*J. Physical Chem.*, 1918, **22**, 22—43. ·Compare this vol., ii, 40).—A discussion of false equilibria in reference to the poisoning of catalysts by the adsorption of one or other of the products of reaction. Such adsorption will cause the reaction to slow down, and it may be brought practically to a standstill. In these circumstances, an apparent or false equilibrium is reached which will depend on the relative amount of the catalyst present. It is probable that molten sulphur catalyses, the reaction between hydrogen and sulphur, and that hydrogen sulphide acts as a poison towards the catalyst. A similar effect is supposed to obtain in the reaction between hydrogen and selenium.

Enzyme reactions are in many cases affected by the products of reaction, in that a large quantity of enzyme is required to complete the reaction. In such cases, false equilibria are set up which may be explained in terms of the poisoning of the enzyme by one or other of the reaction products.   H. M. D.

The Variations in the International Tables of Atomic Weights. TH. RENARD (*J. Chim. phys.*, 1917, **15**, 541—548).— A brief discussion of the revisions made of the various atomic weights by the International Committee since 1903. The author advocates the use of the rounded-off values suggested by Guye (compare A., 1916, ii, 386).   W. G.

Hydrogen Isotopy. A. E. LACOMBLÉ (*Chem. Weekblad*, 1918, **15**, 38—40).—Polemical. A criticism of the views expressed by Scheringa (*ibid.*, 1917, **14**, 953) on the relationship of Prout's hypothesis to the periodic system.   A. J. W.

Prout's Hypothesis and the Periodic System. K. SCHERINGA (*Chem. Weekblad*, 1918, **15**, 221).—A reply to Lacomblé (preceding abstract).   A. J. W.

The Exchange of Energy in the Collisions between Slowly-moving Electrons and Molecules of Gases. G. HERTZ (*Ber. Deut. physikal. Ges.*, 1917, **19**, 268—288).—A theoretical paper in which the laws governing the exchange of energy between colliding electrons and molecules are discussed in reference to atomic and molecular structure. From the available data for helium, it is calculated that the loss of energy in the collision between an electron and a helium atom is 0·00027 times the energy of the electron. This result is very nearly the same as that which is derived on the assumption that the laws of collision are those governing collisions between elastic spheres, and from the close

agreement the conclusion is drawn that the energy lost by the electron is represented by the increase in the kinetic energy of the helium atom.   In the case of hydrogen, however, the loss of energy is found to be much greater, namely, 0.06 of the energy of the electron, and it would seem that the collision of an electron with a hydrogen molecule is accompanied by an increase in the internal energy of the molecule.

The movement of electrons in gases at higher pressures and the influence of small quantities of impurities on the effects produced are also discussed from the point of view of the author's theory.

<div align="right">H. M. D.</div>

Valency Centres.   III.   The Periodic System.   O. HINS-BERG (*J. pr. Chem.*, 1917, [ii], **96**, 166—173.   Compare A., 1916, i, 725 ; 1917, ii, 173, 461).—As explained in the earlier papers, the atoms of the elements lithium, glucinum, boron, and carbon are assumed to possess one valency centre, the chemical valency of which ranges from one to four, the maximum being attained at carbon ; in the remaining elements of the first group, the atoms contain two valency centres, one being quadrivalent throughout and the other gradually increasing in valency from 1 to 4, so that the surplus or normal valency falls in the order 3, 2, 1, 0 for nitrogen, oxygen, fluorine, and neon respectively.   Similar differences exist in the second series of the periodic system ; a single valency centre or atomic nucleus is present in the first four members, but at the fifth element, namely, phosphorus, a second valency centre enters, and the remainder of the elements of the series up to argon contain the two atomic nuclei which in the last element just satisfy one another and leave the element without free valency ; contrary to the earlier opinion, chlorine probably contains only two valency centres, this view receiving support from the similarity in the general properties of the chlorides and cyanides, and the analogy between the intra-atomic structure of the chlorides and the intra-molecular structure of the cyanides, for example, $\cdot\frown\cdot$–Ag for silver chloride and N–C–Ag for silver cyanide.   In the next series, a different type is encountered ; the assumption is made that in these elements a sexavalent atomic nucleus is present, in which the active valency increases by units from potassium up to the maximum of six, which is attained at chromium ; the atoms of the succeeding elements, manganese, iron, cobalt, and nickel, include an additional valency centre which possesses an additional free valency at each element named, so that the maximum possible valency for these metals is 7, 8, 9, and 10 respectively, the maximum apparently being attained in iron carbonyl, $Fe(CO)_4$, with octavalent iron ; in the case of cobalt, the full possible nonavalency is never reached, the differential valency, or the difference between the valency of the sexavalent and tervalent nuclei supplying the maximum ; with nickel also the differential valency has a value 2, in agreement with the composition of most of the compounds,

although in nickel carbonyl, $Ni(CO)_4$, the atom appears to attain octavalency, but, however, is still short of decavalency. The metallic nature of the whole of the ten elements of this third series is ascribed to the presence of the sexavalent atomic nucleus. Copper is regarded as a transition element between the third and fourth series, and therefore probably abnormal; from zinc onwards, the members of the fourth series fall into a normal group, the valency of the first atomic nucleus gradually increasing in valency until quadrivalent germanium is reached; after this point, the atoms of this series contain a second atomic nucleus the valency of which gradually increases from unit value in arsenic to 4 in krypton, the latter therefore being devoid of free valency. For the present, the theory is extended only as far as the fifth and sixth groups; the elements of the former contain as their essential characteristic a sevavalent atomic nucleus which exerts its full effect in molybdenum, the last four elements of the group (one unknown) including an additional nucleus, but the final elements, namely, rhodium and palladium, exert only their differential valency. Silver, like copper, is probably an abnormal transition element. The sixth series, from cadmium to xenon, is normal, and corresponds with the zinc–krypton group.   D. F. T.

Inorganic Chemistry.

The Hydrides of the Metalloids. R. DE FORCRAND (*J. Chim. phys.*, 1917, **15**, 517—540).—An elaboration of work already published (compare A., 1905, ii, 696) and a discussion of Berthoud's work on this subject (compare A., 1917, ii, 237).   W. G.

Hydrogen Peroxide as a Reducing Agent. M. KLEINSTUCK (*Ber.*, 1918, **51**, 108—111).—Silver chloride, suspended in potassium hydroxide solution, is quickly reduced by hydrogen peroxide according to the equation $2AgCl + H_2O_2 + 2KOH = 2Ag + O_2 + 2KCl + H_2O$.

Carbonyl chloride and phenyl carbonate also react with alkaline hydrogen peroxide, and so does a saturated solution of potassium hydrogen carbonate if kept at 100° in a pressure bottle. The distillate obtained by passing steam through the products reduces ammoniacal silver oxide, and is therefore said to contain formaldehyde. The author sees in these reactions a new interpretation of the assimilation of carbon dioxide by plants, thus: $H_2CO_3 + H_2O_2 = CH_2O + H_2O + 3O$. [See also *Ind.*, April.]   J. C. W.

Variations of the Density of Air and the Loomis-Morley Law. PH. A. GUYE (*J. Chim. phys.*, 1917, **15**, 561—566).—A study of the results obtained by various workers for the weight of a normal litre of air, in which it is shown that the results, taken as

a whole, verify the qualitative experimental relation, stated by Loomis and Morley, between the density of the air and the barometric pressure. The most probable explanation of such variations in density is based on the presence in the air of varying quantities of dust, invisible under the ultramicroscope. The mean of the most modern determinations gives the value $1·2928$ grams as the weight of a normal litre of air.   W. G.

Portable Hydrogen Sulphide Generator. W. Faitoute Munn (*J. Ind. Eng. Chem.*, 1918, **10**, 130—131).

—A wide glass tube has two bulbs formed at its lower end, the bottom bulb being provided with a draw-off tap. A perforated lead plate is fitted at the constriction between the bulbs (a piece of glass tubing in the lower bulb acts as a support for the plate) and ferrous sulphide is filled into the upper bulb. The acid reservoir consists of a large bulb, the stem of which passes through a cork closing the top of the wide glass tube and extends to the bottom of the lower bulb. A tapped exit tube for the gas is placed near the top of the wide tube, and this exit tube is fitted with a small washing tube.   W. P. S.

Automatic Hydrogen Sulphide Stopcock. Carl H. Classen (*J. Ind. Eng. Chem.*, 1918, **10**, 131—132).

—To the delivery tube of the hydrogen sulphide apparatus is attached a length of rubber tubing in which is inserted a glass " pearl " made from glass tubing having a diameter slightly larger than that of the rubber tubing. When the rubber tubing over the " pearl " is compressed between the finger and thumb, a channel for the flow of the gas is formed between the glass and the rubber.   W. P. S.

Chloro- and Bromo-aminosulphonic Acids. Wilhelm Traube and E. von Drathen (*Ber.*, 1918, **51**, 111—115).

—Solutions of potassium aminosulphonate and hypochlorous acid in equivalent proportions react in the cold to form *potassium chloroaminosulphonate*, $NHCl·SO_3K$, which may be isolated by evaporating the mixture to a small bulk, in a high vacuum, at as low a temperature as possible and precipitating with alcohol. The salt forms limpid, hygroscopic crystals, and is comparatively stable. When warmed with mineral acids, hydrolysis takes place according to the equation $NHCl·SO_3H + H_2O = NH_2Cl + H_2SO_4$. The corresponding *barium* salt is not so stable, but *potassium bromoaminosulphonate* is very similar.

Similar salts may be prepared by the interaction of free aminosulphonic acid and metallic hypochlorites. Alkylaminosulphonates apparently give very unstable products, for evolution of gas is noticed as soon as hypochlorous acid is added.

There are indications that a double amount of hypochlorous acid produces less stable dichloroaminosulphonates.   J. C. W.

Rate of Hydrolysis and Electrical Conductivity of Hypophosphoric Acid Solutions. R. G. Van Name and Wilbert J. Huff (*Amer. J. Sci.*, 1918, [iv], **45**, 103—118).

—The iodometric

method for the estimation of phosphorous acid in presence of hypophosphoric acid (this vol., ii, 128) has enabled the authors to investigate the rate of hydrolysis of the latter acid. The data obtained at 25° and 60° show that in dilute solutions containing hydrochloric acid as catalyst the hydrolysis proceeds in accordance with the equation for a unimolecular change. The velocity coefficient increases much more rapidly than the hydrogen ion concentration. The temperature coefficient for 10° is 2·7. The fact that the hydrolysis follows a unimolecular law is in favour of the formula $H_4P_2O_6$ rather than H_2PO_3 for hypophosphoric acid, for the production of phosphorous and phosphoric acids would require the interaction of two molecules of acid if it had the simpler formula.

For the conductivity measurements, pure solutions of the acid were prepared from lead and copper hypophosphate by the action of hydrogen sulphide at low temperatures. The metallic sulphides were filtered off and the excess of hydrogen sulphide removed by a current of air. The conductivity of the solutions after complete hydrolysis was also determined.

The molecular conductivity at 25° referred to the formula $H_4P_2O_6$ increases from $\Lambda = 384\cdot7$ at $v = 32$ to $\Lambda = 629\cdot3$ at $v = 1024$. After hydrolysis, the conductivity of the stronger solutions is diminished, whilst that of the more dilute solutions is increased.

Attention is directed to the resemblance between the properties of hypophosphoric acid and pyrophosphoric acid. This resemblance is found in the conductivity of the solutions, in the behaviour towards indicators, and in their solubility relations, and may be adduced in support of the formula $H_4P_2O_6$ for hypophosphoric acid.　　　　　　　　　　　　　　　　　　　　H. M. D.

Preparation of Amorphous Boron. WILHELM KROLL (*Zeitsch. anorg. Chem.*, 1918, **102**, 1—33).—The paper gives the results of numerous experiments on the reduction of boron compounds. Aluminium is unsuitable. Sodium yields mixtures of the lower oxides of boron mixed with boride. Calcium produces only borides. Magnesium may be used for the reduction of boric acid, but the product contains more than 3% Mg in the form of insoluble boride. The halogen compounds of boron can be reduced by potassium, sodium, magnesium, and aluminium; in each case, borides of the metal are formed as well as free boron. The purest boron is obtained by the reduction of boron chloride with hydrogen in the high tension electric arc. Red phosphorus does not reduce boric acid.

When boric acid is heated with magnesium nitride, a *boron nitride*, probably B_3N, is produced. Boron nitride, BN, can be conveniently prepared from boric acid and calcium cyanamide.

When boron chloride is passed over red phosphorus in the presence of oxygen, a *phosphate*, $2B_2O,P_2O_5$, is formed. Other phosphates appear to exist.

The original contains details as to analytical processes regarding compounds of boron. [See, further, *Ind.*, 148A.]　　　R. V. S.

Nomenclature of Silicon Compounds. ALFRED STOCK (*Ber.*, 1917, **50**, 1769—1771. Compare A., 1917, ii, 204).—The author again emphasises the fact that very little chemical similarity exists between silicon and carbon compounds of the same structure, and proposes to abandon the nomenclature of carbon chemistry as far as possible. For example, the radicle –SiO·OH in no way resembles a carboxyl group, and therefore the term "hydroxyoxo" is suggested in such a case.   J. C. W.

Silicon Hydrides. II. Bromination of Monosilane, SiH₄. SiH₃Br and SiH₂Br₂. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1917, **50**, 1739—1754. Compare A., 1916, ii, 319). —The experiments, fully described in this paper, had for their object the bromination of pure silane under conditions favourable to the production of the lower bromides. Under ordinary conditions, the reaction between bromine and silane is very violent, but if an excess of the gas is led into a large vessel on the walls of which solid bromine is deposited, and the temperature is maintained at about $-80°$ to $-70°$, the mono- and di-substitution products can be obtained comparatively free from $SiHBr_3$ and $SiBr_4$.

The apparatus employed is very elaborate (see A., 1917, ii, 442) and the manipulation is a matter of considerable difficulty. For details of the preparations and final fractionations, the original should be consulted.

Bromomonosilane, SiH_3Br, is a colourless gas with a pungent odour, at the same time reminiscent of monosilane. It has m. p. $-94°$, b. p. $+1·9°/760$ mm., D^0 $1·533$, and molecular latent heat of vaporisation $5·83$ Cal. It may be preserved over mercury for some time, but it detonates on exposure to the air, giving silicic acid and brown silicon. It reacts with cold water according to the equation $2SiH_3Br + H_2O = 2HBr + (SiH_3)_2O$ (see following abstract), whilst it may be analysed by measuring the volume of hydrogen produced under treatment with 30% sodium hydroxide, according to the equation $SiH_3Br + 3NaOH = 3H_2 + NaBr + Na_2SiO_3$.

Dibromomonosilane, SiH_2Br_2, is a colourless, mobile, highly refractive liquid, m. p. $-70·1°$, b. p. $66°/760$ mm. (extrapolation; highest recorded value, $18°/123$ mm.), D^0 $2·17$, molecular latent heat of vaporisation $7·41$ Cal. In carefully dried vessels, it may be kept for a long time, but it inflames in the air. It is very sensitive to moisture, being decomposed into hydrogen bromide and a solid, $(SiH_2O)_x$. Alkalis decompose it according to the equation $SiH_2Br_2 + 4NaOH = 2H_2 + 2NaBr + Na_2SiO_3 + H_2O$.
                                              J. C. W.

Silicon Hydrides. III. Disiloxane, (SiH₃)₂O; Tetrachloromonosilane, SiCl₄; Hexachlorodisiloxane, (SiCl₃)₂O. ALFRED STOCK, CARL SOMIESKI, and ROBERT WINTGEN (*Ber.*, 1917, **50**, 1754—1764).—When bromomonosilane is shaken with water, it changes into *disiloxane*, $(SiH_3)_2O$, the preparation and purifica-

tion of which are now described. It is a colourless, odourless gas which does not inflame spontaneously, but burns with a brilliant light, giving a white smoke and a deposit of brown silicon. It has m. p. $-144°$, b. p. $-15\cdot2°$, D^{-80} $0\cdot881$, molecular latent heat of vaporisation $5\cdot63$ Cal. (compare SiH_4, $3\cdot03$; Si_2H_6, $5\cdot18$; Si_3H_8, $7\cdot13$; Si_4H_{10}, $9\cdot18$ Cal.). The m. p. and b. p. are lower than the constants for the parent hydride, Si_2H_6 (m. p. $-132\cdot5°$, b. p. $-15°$), which is the reverse of the relationships between ethane and dimethyl ether. It only decomposes rapidly under the influence of heat when raised to redness. Submitted to a discharge of electric sparks, it slowly yields pure hydrogen. When mixed with oxygen, it inflames or explodes at once, the alteration in volume being in accordance with the equation $(SiH_3)_2O + 3O_2 = 2SiO_2 + 3H_2O$. It is not appreciably soluble in water, but soon decomposes into hydrogen and insoluble products, like $(SiH_2O)_x$, etc. With sodium hydroxide, however, decomposition is complete, according to the equation $(SiH_3)_2O + H_2O + 4NaOH = 2Na_2SiO_3 + 6H_2$, which may be applied in the analysis of the gas.

Disiloxane and chlorine react very vigorously at $-125°$; the primary product, hexachlorodisiloxane, may be isolated, but most of it decomposes according to the equation $4(SiCl_3)_2O = 2SiO_2 + 6SiCl_4$, and some brown silicon is even formed as well. "*Tetrachloromonosilane*" (silicon tetrachloride) has m. p. $-68\cdot7°$, b. p. $56\cdot8°/760$ mm., molecular latent heat of vaporisation $7\cdot19$ Cal., and "*hexachlorodisiloxane*" is now found to have m. p. $-33°$ and b. p. $137°/760$ mm.

It is an interesting fact that disiloxane is the first volatile compound of silicon, hydrogen, and oxygen. Many derivatives, with the same elements, are known, such as "silicoformic anhydride," $(O\colon SiH)_2O$, but these must assuredly be polymerides, whereas alkyl, alkoxyl, and similar derivatives of the true monomeric type, for example, $(SiR_3)_2O$ and $[Si(OR)_3]_2O$, have frequently been prepared (compare Martin and Kipping).

Apparently, the compound $SiH_3\cdot OH$, which would be the primary product of the action of water on SiH_3Br, is very unstable. It is noteworthy that the alkyl derivatives, $SiR_3\cdot OH$, also change into oxides readily, but the alkyl groups do confer a measure of stability on them, for hexaphenyldisiloxane, $(SiPh_3)_2O$, changes back into $SiPh_3\cdot OH$ on boiling with alcoholic potassium hydroxide (Kipping and Lloyd, T., 1901, **79**, 455). J. C. W.

Silicon Hydrides. IV. Oxomonosilane (Protosiloxane). ALFRED STOCK, CARL SOMIESKI, and ROBERT WINTGEN (*Ber.*, 1917, **50**, 1764—1769).—Dibromomonosiloxane reacts with water to form hydrogen bromide and a volatile compound, which is very probably *oxomonosilane (protosiloxane)*, SiH_2O. The authors have not been able to isolate this, as it is about as volatile as the hydrogen bromide solution, and, furthermore, polymerises most readily, so that after a few distillations the whole of the original silicon is found in the insoluble residues. The *polymeride* is an amorphous, white solid,

which is stable at 300° (vacuum) or in contact with boiling water, but inflames in the air or chlorine, and reacts with sodium hydroxide according to the equation $(SiH_2O)_x + 2NaOH \longrightarrow 2H_2 + Na_2SiO_3$.   J. C. W.

Proof of the Production of Water in the Formation of Salts from Acid and Base. W. FRANCK (*Zeitsch. physikal Chem. Unterr.*, **30**, 147; from *Chem. Zentr.*, 1917, ii, 358—359). —In the experiment described by Zeitler (A., 1917, ii, 463), calcium or barium hydroxide should be used, as the alkali hydroxides are never anhydrous.   R. V. S.

The System Lithium Sulphate–Lithium Chloride–Water at 30°. F. A. H. SCHREINEMAKERS and G. M. A. KAYSER (*Chem. Weekblad*, 1918, **15**, 120—121).—The solubility of lithium sulphate in water is much diminished by the presence of lithium chloride.   A. J. W.

The Necessity for Applying a New Correction to the Atomic Weight of Silver. PH. A. GUYE (*J. Chim. phys.*, 1917, **15**, 549—560).—The author discusses the various sources of error, due to the presence of occluded gases and the adherent pellicle of moisture on the metal, in the atomic weight determinations of silver. On the basis of recent work (compare A., 1916, ii, 432), he considers that the atomic weight of silver should be revised to 107·87, and that the correct values for the halogens should be $Cl = 35·461$, $Br = 79·925$, $I = 126·915$.   W. G.

Metallographic Investigation of the System Zinc and Selenium. MASUMI CHIKASHIGE and ROKURO KUROSAWA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 245—248).—When zinc and selenium are heated together at a sufficiently high temperature, the compound ZnSe is formed. Zinc selenide has a brilliant yellow colour, D^{21} 5·29, and does not fuse up to 1100°. The fused elements are not appreciably miscible, and the selenide does not dissolve in either. If a fused mixture is allowed to cool, the two free elements and the compound are detectable in the solidified product when examined under the microscope. [See *Ind.*, 153a.]
                                                    H. M. D.

Metallographic Investigation of the System Cadmium and Selenium. MASUMI CHIKASHIGE and RIICHI HIKOSAKA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 239—244).—Cadmium and selenium combine to form the compound CdSe, which is infusible up to 1350° and has D^{16} 5·81. The reaction between the elements begins to be appreciable at about 360°, and its velocity increases with rise of temperature. The cadmium selenide does not dissolve in either of the molten elements, which are themselves practically immiscible. When, therefore, a mixture of the two elements is fused and cooled, the product consists of a mixture of cadmium selenide, cadmium, and selenium, which are readily recognised under the

microscope. The proportion of the compound in the product depends on the temperature to which the mixture has been heated and on the length of the period of heating. [See *Ind.*, 153A.]

H. M. D.

The System, Copper Chloride–Lithium Chloride–Water at 30°. F. A. H. SCHREINEMAKERS and (MISS) A. C. NOORDUYN (*Chem. Weekblad*, 1918, **15**, 118—120).—An application of Schreinemakers's graphic method to solutions containing cupric and lithium chlorides. A. J. W.

The Critical Constants of Mercury. E. ARIES (*Compt. rend.*, 1918, **166**, 334—337).—Using the formula previously given (compare this vol., ii, 61) for monatomic vapours, and taking the known vapour pressures of mercury at different temperatures, the author calculates the critical temperature of mercury as 1077° and the critical pressure as 420 atmos., these values being a close approximation to the correct figures. W. G.

Preparation, Properties, and Analysis of "White Precipitate." I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 208—218).—A comparison of the methods for preparing "white precipitate" given in the Dutch, German, English, Belgian, Swiss, and U.S.A. pharmacopœias. The author is of opinion that the Dutch method is the most satisfactory. [See, further, *Ind.*, April.]

A. J. W.

The Space Lattice of Aluminium. P. SCHERRER (*Physikal. Zeitsch.*, 1918, **19**, 23—27).—The method described by Debye and Scherrer (A., 1917, ii, 437) for the X-ray examination of crystal structure has been applied to finely powdered aluminium. The interference photographs afford evidence that aluminium forms cubic crystals, and that the atoms are arranged according to a simple face-centred lattice. Measurements of the interference patterns give 4.07×10^{-8} cm. for the length of the edge of the elementary cube. The corresponding values obtained from previous investigations are: copper 3.61, silver 4.06, gold 4.07, and lead 4.91×10^{-8} cm.

In spite of the close agreement between the values of the lattice constants and of the atomic volumes for aluminium and gold, the two metals do not form a complete series of mixed crystals. This is attributed to the preponderating influence of chemical affinity.

H. M. D.

The Effect of Great Hydrostatic Pressure on the Physical Properties of Metals. ZAY JEFFRIES (*J. Inst. Metals*, 1917, **18**, 243—252).—The statement of Hanriot (A., 1913, ii, 112) that metals subjected to hydrostatic pressures of the order of 10,000 kilos. per sq. cm. are permanently hardened without deformation, is contrary to modern views on hardness. A repetition of the experiments, using aluminium and an alloy of aluminium and copper,

immersed in light petroleum under pressures up to 12,400 kilo. per sq. cm., shows that no increase in hardness is produced. Hanriot used vaselin, which becomes solid under very high pressures, so that the pressure applied is not hydrostatic. Experiments with the same metals show that a degree of cold deformation, insufficient to cause a noticeable change in the dimensions, produces a marked increase in the hardness as determined by the scleroscope. This explanation is more probable than that of the occurrence of allotropic change in the metal. [See *Ind.*, April.]

C. H. D.

Metallographic Investigation of the System, Aluminium and Selenium. MASUMI CHIKASHIGE and TSUGIJI AOKI (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 249—254).—Cooling curve observations show the formation of a compound, Al_3Se_4, which melts at about 950°. The formation of this compound by heating the two elements together is frequently accompanied by an explosion unless the mixture contains more than 90% of selenium. The compound crystallises out from all fused mixtures of the two elements, and in accordance with this, the two branches of the compound curve on the freezing-point diagram cover the whole of the region from pure aluminium to pure selenium. The eutectics are therefore very nearly coincident with the freezing points of the two elements. The microcrystalline structure of solidified mixtures is in agreement with the thermal data.

Aluminium selenide decomposes in contact with moist air with the formation of hydrogen selenide and aluminium hydroxide. [See *Ind.*, 153A.]   H. M. D.

Metallographic Investigation of the System, Tellurium and Aluminium. MASUMI CHIKASHIGE and JITSUZO NOSÉ (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 227—232).—When aluminium and tellurium are heated together, combination takes place with explosive violence, and the compound Al_2Te_3, m. p. 895°, is formed. This telluride forms mixed crystals with tellurium, the series extending from the pure compound (12·4% by weight of aluminium) to a mixture which contains 4·4% of aluminium. On cooling, the α-mixed crystals undergo transformation into β-mixed crystals. The temperature at which this conversion takes place diminishes with increase in the tellurium content, and for the saturated α-mixed crystals falls to 541°. The β-mixed crystals and tellurium co-exist at the eutectic temperature 414°, the eutectic mixture containing 2·8% of aluminium.

The freezing-point curve of the compound Al_2Te_3 on the aluminium side is terminated by a eutectic point, in which the telluride and aluminium co-exist in equilibrium. The eutectic mixture contains 97% of aluminium and the eutectic temperature is 621°.

The conglomerates, consisting of the telluride or aluminium and the eutectic, undergo transformation when the temperature has

fallen to 551°, with the formation of Al_5Te, according to the equation $Al_2Te_3 + 13Al = 3Al_5Te$.

The telluride, Al_2Te_3, is energetically decomposed by water or by contact with moist air, with the formation of hydrogen telluride and aluminium hydroxide, according to the equation $Al_2Te_3 + 3H_2O = 3TeH_2 + Al_2O_3$. The compound Al_5Te is less readily decomposed, but hydrogen telluride is liberated in contact with water, the reaction being possibly represented by $Al_5Te + H_2O + O_2 = TeH_2 + Al_2O_3 + 3Al$.

Microphotographs are given which afford evidence in support of the results obtained by the thermal analysis of the system. [See *Ind.*, 153A.] H. M. D.

A Criterion for Allotropic Transformations of Iron at High Temperatures. KÔTARÔ HONDA (*Sci. Rep. Tohoku Imp. Univ.*, 1917, **6**, 213—217).—The transformations of iron consist in part of allotropic changes which take place at a definite temperature and of gradual changes in which the equilibrium condition is a continuous function of the temperature. The available data relating to these transformations show that A_2 is of the second type, whilst A_3 and A_4 are allotropic changes.

In the case of carbon steels, there are in addition the changes designated by A_0 and A_1, the former representing a gradual change in cementite, and the latter a eutectic transformation of cementite and ferrite which occurs at a definite temperature. H. M. D.

The Micro-structure of Commercially Pure Iron between Ar_3 and Ar_2. W. J. BROOKE and F. F. HUNTING (*J. Iron Steel Inst.*, 1917, **96**, 233—250).—Armco iron, a basic open-hearth product containing as much as 99·84% Fe, passes through a characteristic brittle range between 900° and 800°, but only during cooling, no change being observed within this range during heating. Quenching experiments show that a eutectic or eutectoid structure appears between these temperatures, but is absent either above or below the brittle range. This constituent resembles pearlite in structure, but is not related to the carbon content, and is also independent of the quantity of oxide in the iron. Heating in hydrogen is without influence on the structure. Similar results are obtained with Swedish iron containing about 0·04% of carbon. [See, further, *Ind.*, 1917, 1096.] C. H. D.

The Nature of Subsidiary Valencies. XVII. Prediction of the Decomposition Temperatures of Ammines. FRITZ EPHRAIM and ELIAS ROSENBERG (*Ber.*, 1918, **51**, 130—136).—It was recently shown that the ratio of the temperatures of dissociation for certain pairs of compounds of two elements is roughly constant (A., 1917, ii, 531). If the dissociation points of a number of compounds of one element are known, and the ratio has been determined in the case of one pair of corresponding compounds for another element, then the dissociation temperatures of all the other compounds of the second element can be predicted. This is illus-

trated further in the case of the hexammines of nickel and cobalt salts. The ratio, or "temperature-modulus of the tension," calculated from the dissociation temperatures of the iodides, is Ni/Co, $1/1.075$ (A., 1912, ii, 546). Dividing the known temperatures for other nickel salts by 1.075, therefore, gives approximately the dissociation points for the corresponding cobalt salts. In the cases of the hexammines of the bromides, nitrates, dithionates, chlorides, sulphates, acetates, and hydrogen carbonates (descending order of stability), the calculated values agree with the observed ones within the limits of the experimental errors.

Most of the hexammines mentioned have been described before (A., 1913, ii, 496, 1061), but the following are new: *cobalthexammine nitrate*, by warming the crystalline nitrate in ammonia gas, *dithionate, hypophosphite, formate*, and *acetate*; the dissociation temperatures are respectively 160°, 157·5°, 51°, 21·5°, and 55·5°.   J. C. W.

Metallographic Investigation of the System, Selenium and Antimony. MASUMI CHIKASHIGE and MASASUKE FUJITA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 233—237).—Cooling-curve data show that antimony and selenium form a compound, Sb_2Se_3, melting at 572°. With antimony, the compound forms a eutectic mixture containing 46·5% of selenium, the eutectic temperature being 497°. The eutectic on the selenium side of the compound corresponds very nearly with pure selenium melting at 211°.

Microscopic investigation of solidified mixtures of the two elements confirm the results obtained in the thermal analysis. [See *Ind.*, 153A.]   H. M. D.

Mineralogical Chemistry.

Composition of Seleniferous Sulphur. GLENN V. BROWN (*Amer. Min.*, 1917, **2**, 116—117. Compare A., 1916, ii, 531).— Examination of further specimens of so-called selen-sulphur from various localities (Sicily, Lipari, and New Zealand) by the method of W. Smith (A., 1915, ii, 839) shows the presence of only small amounts of selenium (trace—0·298%). The depth of colour of the material bears no relation to the amount of selenium present; pale yellow specimens may contain more of this element than deep brown ones.   L. J. S.

Epiboulangerite from Montana. EARL V. SHANNON (*Amer. Min.*, 1917, **2**, 131—132).—Bunches of steel-grey needles and fibrous masses occur with quartz and granular blende in the Iron Mountain mine, near Superior, Montana. Small grains and needles are also scattered through the blende. Associated minerals

in small amounts are chalybite, pyrites, and sericite. The fibres are moderately brittle and break across at right angles; the streak is blackish lead-grey. D 6·303. A partial analysis gave Pb 52·74, Sb 20·85%. From these characters, the mineral is provisionally identified as epiboulangerite.   L. J. S.

Mullanite, a New Member of the Jamesonite Group, from Two Localities. EARL V. SHANNON (*Amer. J. Sci.*, 1918, [iv], **45**, 66—70).—In the Iron Mountain mine near Superior, Montana, the new mineral occurs with epiboulangerite (preceding abstract), from which it is indistinguishable in appearance; but it is readily distinguished by its brownish-black streak, that of the epiboulangerite being greyish-black. It here forms long, parallel, steel-grey fibres around and enclosed in a crystal of quartz. In the Gold Hunter mine, near Mullan, in Idaho, forty miles W.N.W. of the former locality, the mineral occurs with quartz and chalybite as fine, matted, wool-like masses of dark grey fibres, and as a compact, steel-grey, fibrous material. The needles are usually flattened and are deeply striated longitudinally; they are terminated by the basal plane, and are probably orthorhombic ($a : b = 1 : 0.835$) with the three pinacoidal cleavages. The thinner fibres are very flexible, whilst the thicker ones are quite brittle. Analysis I, mean of two of material from the Iron Mountain mine, and II, from the Gold Hunter mine, agree with the formula $5PbS,2Sb_2S_3$, corresponding with the silver-lead diaphorite.

	Sb.	As.	Pb.	Ag.	Cu.	Fe.	S.	Total.	Sp. gr.
I.	25·71	0·25	55·05	nil	nil	trace	18·82	99·83	6·274*
II.	24·67	0·64	53·33	nil	nil	1·47†	18·11	98·22	6·407

* Probably low.   † Representing chalybite 3·4% present as impurity.

L. J. S.

Occurrence of Chalmersite, $CuFe_2S_3$, in the Ore Deposits of Prince of Wales Sound, Alaska. BERTRAND L. JOHNSON (*Econ. Geol.*, 1917, **12**, 519—525).—This mineral, previously known only as minute crystals from Brazil (A., 1902, ii, 267; 1906, ii, 553), has been found in considerable quantities at eight different localities in the Ellamar district and on Knight Island, in Prince of Wales Sound, where it has been mined as an ore of copper. It is massive, very pale yellow, and shows a conspicuous cleavage with a satiny sheen. It is strongly magnetic, and this property enables it to be separated from the copper-pyrites with which it is intimately intergrown. Analyses by E. T. ALLEN agree with the formula $CuFe_2S_3$.

Cu.	Fe.	S.	Sp. gr.
22·67—23·83	40·70—41·92	35·09—35·30	4·04

L. J. S.

Chalcedony Mistaken for an Iron Sulphate Mineral. EDGAR T. WHERRY and MILTIADES L. GLENN (*Amer. Min.*, 1917, **2**, 6—7).—Two specimens of orange-brown botryoidal material had

been for many years labelled as glockerite in the U.S. National Museum. I is from Pinos Altos, New Mexico, and II from Black Hawk, Colorado. When examined, they were found to be chalcedony, and this is confirmed by analyses I and II. The ferric sulphate is not present as visible enclosures, nor is it extracted by acids; it must be present as sub-microscopic inclusions.

	SiO_2.	Fe_2O_3.	SO_3.	$H_2O < 110°$.	$H_2O > 110°$.	Total.	Sp. gr.	n.
I.	94·37	3·10*	1·47	trace	1·86	100·80	2·57	1·530
II.	93·94	1·58	1·00	0·65	2·59	99·76	2·55	1·525

* Including a minute amount of pyrites.

For pure chalcedony $D = 2·60$ and $n = 1·537$; as shown above, with increasing water there is a corresponding decrease in the values for the density and refractive index.   L. J. S.

Massicot and Litharge, the Two Modifications of Lead Monoxide. ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 18—19).— Natural specimens of 'massicot' from Austria and from Kern Co. and San Bernardino Co., California, consist of minute brownish-red scales built up of two minerals with distinct optical properties. The central portion of the plates consists of the yellow orthorhombic modification (nearly colourless under the microscope, optically biaxial and positive, $\beta = 2·61$, birefringence very strong), and the borders of the red tetragonal modification (yellowish-orange under the microscope, optically uniaxial and negative, $\omega = 2·64$, birefringence very strong). It is proposed to restrict the name litharge to the former and massicot to the latter. The border of massicot is probably an inversion product of the litharge. (Compare A., 1915, ii, 59).   L. J. S.

Nomenclature of the Lead Monoxide Minerals. E. T. WHERRY (*Amer. Min.*, 1917, **2**, 19).—The mineralogical term massicotite for a mineral corresponding with the artificial product massicot was used by D'Achiardi in 1883. Now that the orthorhombic modification of lead monoxide has been recognised as a mineral (see preceding abstract), the name *lithargite* is suggested for the second species.   L. J. S.

Xanthosiderite from Schendlegg, Lower Austria : Formation of Brown "Glaskopf." H. LEITMEIER and M. GOLDSCHLAG (*Centr. Min.*, 1917, 473—477).—Near the foot of the Raxalp, in Lower Austria, are deposits of iron ore consisting of chalybite carrying small amounts of copper-pyrites. In the level of the Schendlegg mine, the walls are coated with a reddish-brown, unctuous, colloidal material of recent formation. After drying in the air for a few weeks, this shows a concentric, shelly structure and brown colour; the streak is yellowish-brown. Under the microscope, it showed thin scales of brownish-yellow, amorphous material. It then contained 19·70% H_2O, corresponding with $Fe_2O_3,2H_2O$—the formula for xanthosiderite. Of this water, 3·93% is lost over sulphuric acid and 8·16% at 100°. The same

material after exposure to the air for two years still contained the same quantity of water (H_2O 19·11, Fe_2O_3 80·02, SiO_2 0·47%), but it had by that time acquired a dark blackish-brown colour with metallic lustre on the surface and a dark brown streak. Under the microscope, the material was now seen to have a distinct granular structure and to be crystalline. The colloidal material has thus become gradually converted to the crystalline, brown " Glaskopf." L. J. S.

Columnar Manganocalcite from Franklin Furnace, New Jersey. WALLACE GOOLD LEVISON (*Amer. Min.*, 1916, **1**, 5).—This is pinkish-white with a marked columnar structure. It is tough and less brittle than ordinary calcite, and is soluble in cold acid. Analysis gave:

CaO.	MnO.	FeO.	ZnO.	MgO.	CO_2.	Insol.	Total.	Sp. gr.
38·58	11·94	0·22	0·29	4·33	39·70	4·60	99·66	2·81

L. J. S.

Proof that Priceite is a Distinct Mineral Species. ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 1—3).—The friable, chalky priceite from Curry Co., Oregon, and the compact, nodular pandermite from Asia Minor have often been regarded as impure, massive varieties of colemanite. A determination of the optical constants of these minerals proves that pandermite is identical with priceite ($\alpha = 1·572$, $\beta = 1·592$, $\gamma = 1·594$), and that the latter is distinct from colemanite ($\alpha = 1·586$, $\beta = 1·592$, $\gamma = 1·614$). Priceite is triclinic, $5CaO,6B_2O_3,9H_2O$, and colemanite monoclinic, $2CaO,3B_2O_3,5H_2O$. On the other hand, fine-grained specimens (labelled priceite) of hydrous calcium borate from Californian localities were found to be howlite. L. J. S.

Vivianite from the Land Pebble Phosphate Deposits of Florida. THOMAS L. WATSON and STAPLETON D. GOOCH (*J. Washington Acad. Sci.*, 1918, **8**, 82—88).—An examination of a sample of vivianite occurring in a ferruginous or dark yellow, ochreous matrix in a deposit of Florida pebble phosphate. The mineral occurred as light to pale green crystals, D 2·693, an optical examination of which gave the following results: optically ($+$); $2V$ large; dispersion not strong; X is normal to 010; Z makes an angle of $28°30' \pm 1°$ with c. The refractive indices are $\alpha = 1·580 \pm 0·003$; $\beta = 1·598 \pm 0·003$; $\gamma = 1·627 \pm 0·003$. Analysis gave:

FeO.	Fe_2O_3.	CaO.	MnO.	P_2O_5.	TiO_2.	SiO_2.	H_2O (<105°).	H_2O (>105°).	Total.
32·64	9·43	0·02	0·25	29·99	trace	0·12	11·86	15·84	100·15

The presence of ferric oxide in blue vivianite is due to oxidation, and not to inversion. Oxidation takes place rapidly on fine grinding. The matrix in which the vivianite occurs is not a clay, but an earth composed of the hydroxides of iron and aluminium, chiefly the former, phosphates of calcium, iron, and aluminium, and some free quartz. W. G.

Mirabilite from the Isle Royale Mine, Michigan. ALBERT B. PECH (*Amer. Min.*, 1917, **2**, 62—63).—The material, from the Isle Royale copper mine at Houghton, consists of a clear, colourless mass of interlocking fibres with a little clayey matter enclosed. On exposure to the air, it soon crumbles to a white powder. All the water is expelled at 130°. Deducting 5·69% insoluble, the following analysis agrees with the usual formula, $Na_2SO_4,10H_2O$. Mean refractive index, 1·437.

$Na_2O.$	$K_2O.$	CaO.	$SO_3.$	Cl.	$H_2O.$
19·02	0·77	trace	25·37	trace	54·84

L. J. S.

Gilpinite, a New Uranium Mineral from Colorado. ESPER S. LARSEN and GLENN V. BROWN (*Amer. Min.*, 1917, **2**, 75—79).—The mineral occurs as pale greenish-yellow to canary-yellow aggregates of minute, lath-shaped crystals intermixed with gypsum on pitchblende and copper ore from Gilpin Co., Colorado. The crystals are monoclinic, and show two sets of polysynthetic twin-lamellæ. The optical constants are compared with those of zippeite and uranopilite. The mineral is readily soluble in dilute acids; it is difficultly fusible, and becomes black on heating. D > 3·32. The following analysis (19·64% gangue, mainly pitchblende, deducted) gives the formula $RO,UO_3,SO_3,4H_2O$, where R = Cu, Fe, Na_2.

$SO_3.$	$UO_3.$	CuO.	FeO.	PbO.	$Na_2O.$	$K_2O.$	H_2O at 105°.	H_2O at 200°.
15·45	56·72	5·80	4·77	0·82	1·93	0·70	1·66	12·15

A specimen labelled uranopilite from Cornwall was found to have optical characters identical with those of the Colorado mineral, and it is also regarded as gilpinite.   L. J. S.

The Probable Identity of Uranothallite and Liebigite. ESPER S. LARSEN (*Amer. Min.*, 1917, **2**, 87).—Optical examination of three specimens labelled liebigite from Schneeberg, Saxony, and Joachimsthal, Bohemia, and of two specimens labelled uranothallite from the latter locality, gave the following results: optically positive, $2E = 65° \pm 3°$, $2V = 42° \pm 2°$, $\rho > v$, $\alpha = 1·500$, $\beta = 1·503$, $\gamma = 1·537 \pm 0·003$, cleavage normal to α. The single analysis of liebigite (for which the formula was deduced as

$$CaO,UO_3,2CO_2,20H_2O)$$
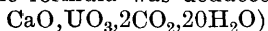
was made in duplicate on only 65 and 85 mg. of material, and although this name has priority, it is rejected in favour of the name uranothallite, which was applied to more completely determined material, and analysed by three authors with the result $2CaO,UO_3,3CO_2,10H_2O$. It is, however, remarked that the original material described as liebigite was not available for optical examination, and it is possible that those examined may really have been uranothallite incorrectly labelled liebigite.   L. J. S.

Pectolite Pseudomorphous after Quartz from West Paterson, N.J. MILTIADES L. GLENN (*Amer. Min.*, 1917, **2**, 43—45).—A small group of crystals collected from a basalt quarry at West Paterson, New Jersey, shows the forms of sharply-developed crystals of quartz, each about $\frac{3}{4}$ inch in diameter. They, however, consist entirely of a compact, fibrous material with the optical characters of pectolite. Analysis of the material gave:

SiO_2.	$Al_2O_3 + Fe_2O_3$.	CaO.	MgO.	Na_2O.	H_2O.	Total.
53·42	0·52	32·63	2·35	7·45	3·77	100·14

L. J. S.

A New Occurrence of Stevensite, a Magnesium-bearing Alteration-product of Pectolite. MILTIADES L. GLENN (*Amer. Min.*, 1916, **1**, 44—46).—The Hartshorn quarry at Springfield, Essex Co., New Jersey, is in a somewhat altered basalt containing in cavities secondary anorthoclase, quartz, calcite, zeolites, datolite, and pectolite. Some of the pectolite is of the usual type as silky radiations of fine needles, but much of it is altered, the colour becoming pinker and the lustre more waxy towards the ends of the fibres. In the most altered material the colour is white to pink, lustre waxy, translucent; the structure is compact, and the material optically isotropic and amorphous, n about 1·50; D 2·15—2·20, H $2\frac{1}{2}$. It is easily fusible to a white enamel, and is decomposed by hydrochloric acid with separation of granular silica. Analysis I is of partly altered material still retaining the pectolite structure, but impregnated by waxy material; and II of the most altered waxy material, apparently homogeneous, although still perhaps containing a few fibres of unaltered pectolite:

	SiO_2.	$Al_2O_3 + Fe_2O_3$.	MnO.	CaO.	MgO.	Na_2O.	$H_2O(>110°)$.	Total.
I.	53·84	1·18	0·13	22·59	9·81	5·59	6·76	99·90
II.	58·03	0·37	0·03	1·61	27·66	3·73	8·45	99·88

These analyses, when arranged in a series with other analyses of altered pectolites ('walkerite' from Corstorphine Hill, Edinburgh, and 'magnesium pektolith' from Burg, Herborn, Germany), show a gradual passage from the monohydrate of pectolite,

$$HNaCa_2(SiO_3)_3 + H_2O,$$
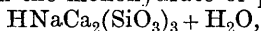
to the monohydrate of talc, $H_2Mg_3(SiO_3)_4 + H_2O$. They show a progressive increase in magnesium and water and a decrease in calcium and sodium. The latter formula, to which anal. II approximates, is given as the composition of stevensite. The alteration has no doubt been brought about by the action of magnesium-bearing solutions derived from the weathering of the basalt. L. J. S.

A Review of Amorphous Minerals. AUSTIN F. ROGERS (*J. Geol. Chicago*, 1917, **25**, 515—541).—The amorphous equivalents of crystalline minerals should be recognised as separate mineral species and given distinctive names. About twenty of the more prominent and well-defined, amorphous minerals (for example, opal, psilomelane, collophane, halloysite, etc.) are discussed. The amor-

phous cadmium sulphide, probably with adsorbed water, CdS,xH_2O, which occurs as a thin, powdery, yellow coating on zinc-blende, is separated from the hexagonal greenockite and named *xanthochroite*.

Intimately associated with the chrysocolla (a microcrystalline or crystallised mineral) of several localties is the amorphous equivalent, to which the name *cornuite* is applied. Cornuite from Copper Mountain, Prince of Wales Island, Alaska, occurs as a banded crust of bluish-green, transparent, glassy material with refractive index 1·549. It is more readily soluble in hydrochloric acid than chrysocolla, and is also somewhat softer. Analysis by G. S. BOHART gave:

CuO.	Al$_2$O$_3$.	SiO$_2$.	H$_2$O.
42·61	0·31	34·13	23·11

Here the ratios of both silica and water are somewhat in excess over those required by the chrysocolla formula, H_4CuSiO_5, and cornuite is probably a solid solution of cupric oxide, silica, and water, $mCuO,nSiO_2,xH_2O$.

The natural hydrocarbons and glasses are discussed under the term mineraloids.   L. J. S.

Nature of the Water in Zeolites. GEORG STOKLOSSA (*Diss. Breslau*, 1917, 64 pp.; from *Chem. Zentr.*, 1917, ii, 420—421). —The author has investigated the following seven minerals, and has found in all cases that the water contained in them is in chemical combination: (1) heulandite from Teigarhorn, in Iceland; (2) skolezite from Iceland; (3) natrolite from Bohemia; (4) harmotome from Strontian; (5) chabasite from Nova Scotia; (6) analcime from the Seiseralp; (7) apophyllite from the Seiseralp. Analyses gave:

	SiO$_2$.	Al$_2$O$_3$.	BaO	CaO.	MgO.	K$_2$O.	Na$_2$O.	H$_2$O.	Total.
1.	59·66	16·37	—	6·33	—	2·35	0·42	14·90	100·03
2.	46·71	25·90	—	13·70	—	—	—	13·64	99·95
3.	46·95	27·06	—	0·27	—	—	15·97	9·58	99·73
4.	48·51	16·44	20·19	—	—	1·59	—	13·79	100·52
5.	48·12	19·27	—	9·63	2·45	3·02	—	16·11	98·59
6.	54·74	23·64	—	0·32	—	—	13·71	8·55	100·96
7.	53·87	—	—	23·85	—	4·81	—	16·24	99·47

       R. V. S.

A New Occurrence of Ptilolite. LOUIS H. KOCH (*Amer. Min.*, 1917, **2**, 143—144).—This species, previously known only from Colorado, is described from Challis, Idaho. The material consists of a soft, fluffy mass of minute fibres coating a layer of chalcedonic silica on a weathered basic igneous rock. Analysis gave:

	SiO$_2$.	Al$_2$O$_3$.	CaO.	MgO.	K$_2$O,Na$_2$O.	H$_2$O.	Total.
I.	81·5	8·2	1·7	0·3	1·0	7·3	100·0
II.	72·3	12·3	2·6	0·4	1·5	10·9	—

The high value for silica is due to the presence of microscopic, spindle-shaped crystals of quartz to the extent of 31⅓%; deducting

this, the results are as under II. Under the microscope the material is seen to consist of well-defined, transparent needles with straight optical extinction; biaxial with large angle and optically negative; refractive indices $\alpha = 1\cdot475$, $\beta = 1\cdot477$, $\gamma = 1\cdot478$. D $2\cdot30$. L. J. S.

A Peculiar Clay from near the City of Mexico. E. W. HILGARD (*Proc. National Acad. Sci., U.S.A.*, 1916, **2**, 8—12).—The material examined consisted of soil samples from certain unproductive tracts of land on the hacienda Santa Lucia. It has the appearance of a dark grey clay, adheres strongly to the tongue, and becomes very plastic with a little water. D $2\cdot25$. When immersed in water it swells up to many times (for one sample as much as thirty-two times) its original volume, forming a coherent, gelatinous mass. The larger part of the material is colloidal, but there are also minute, inseparable grains of calcium and magnesium carbonates. A partial analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Ign.	Insol.	Na_2SO_4.	Na_2CO_3.	NaCl.	Total.
43·00	3·48	1·76	9·06	17·11	19·60	1·83	1·74	0·74	0·12	98·44

The material is thus mainly a hydrated magnesium silicate allied to saponite or sepiolite, but it differs from these in being very readily decomposed by acids, even by dilute acetic acid, and in its exceptionally high absorptive power for water. The name *lucianite* is suggested for this new type of magnesian clay.   L. J. S..

Analytical Chemistry.

Filtering Tube. WILLIAM M. THORNTON, Jun. (*J. Ind. Eng. Chem.*, 1918, **10**, 132).—The stem of a carbon filter tube is provided with a glass tap, and the top of the tube is closed by a rubber stopper, through which pass the stem of a holder for a filter crucible and an exit tube connected with a pump. The carbon tube serves as a small filter flask; the filtrate collected in this tube is discharged by opening the tap and admitting air through a side-tube on the exit tube. The apparatus is convenient for use in dealing with small quantities of liquid. W. P. S.

Preparation of N/100 Permanganate Solutions. J. O. HALVERSON and OLAF BERGEIM (*J. Ind. Eng. Chem.*, 1918, **10**, 119—120).—To prepared permanent $N/100$-permanganate solution 0·40 gram of potassium permanganate is dissolved in 1 litre of re-distilled water, and the solution is heated nearly at boiling point for thirty-six hours under a reflux apparatus. The solution is then cooled, kept overnight, filtered through asbestos, and after three days standardised against $N/50$-oxalic acid solution (0·1261 gram of crystallised oxalic acid per 100 c.c.). The strength of the solution does not vary more than 0·1% per week. [See, further, *Ind.*, 193A.]
W. P. S.

Suggestions on some Common Precipitations. GEORGE H. BROTHER (*J. Ind. Eng. Chem.*, 1918, **10**, 129—130).—The following directions are given for obtaining precipitates which are retained by filter paper of moderately close texture. In the case of barium sulphate, the sulphate solution should contain about 1 c.c. of hydrochloric acid (D 1·2) per 200 c.c.; it should be heated to boiling, treated with about one-half the required quantity of barium chloride solution, added drop by drop, and the remainder of the barium chloride is added after the lapse of five minutes. The mixture is ready for filtration after a further fifteen minutes' digestion.

Calcium oxalate is readily obtained in a crystalline state by treating the boiling solution of the calcium salt with an excess of ammonium oxalate, dissolving the precipitate by adding a very slight excess of hydrochloric acid, then adding ammonia drop by drop until the precipitate has formed again, and keeping the mixture hot for thirty minutes.

For the precipitation of ammonium phosphomolybdate, the phosphate solution is rendered ammoniacal, then acidified with nitric acid, heated to boiling, and treated at this temperature with ammonium molybdate solution. When a phosphate is precipitated with magnesia mixture, the precipitate should be dissolved by the addition of hydrochloric acid, the solution heated to boiling, and ammonia then added slowly until a distinctly crystalline precipitate has formed; the mixture is now cooled, one-fifth of its volume of ammonia (D 0·9) is added, and, after fifteen minutes, the precipitate is collected on a filter.   W. P. S.

Reagents for Use in Gas Analysis. VI. The Absorption of Hydrogen by Sodium Oleate. R. P. ANDERSON and M. H. KATZ (*J. Ind. Eng. Chem.*, 1918, **10**, 23—24. Compare A., 1917, ii, 39).—The sodium oleate reagent containing nickel in suspension, recommended by Bosshard and Fischli for the absorption of hydrogen (A., 1915, ii, 788), is of little use. Amongst the objections to the reagent may be mentioned the time and trouble required for the preparation of the catalyst and the readiness with which it oxidises, the bad keeping properties of the reagent itself, and the slowness of the absorption of the hydrogen. [See further, *Ind.*, 82A.]   W. P. S.

Detection and Estimation of Small Quantities of Free Hydrochloric Acid in the Presence of Chlorides and other Mineral or Organic Acids. M. ENTAT (*Ann. Chim. anal.*, 1918, **23**, 5—7).—Hydrochloric acid may be determined by the electrometric titration method previously described (A., 1917, ii, 268). *N*-Silver nitrate solution is used for titration, and the hydrochloric acid solution should contain 2% of nitric acid.   T. F. B.

Titration of Chlorides by Volhard's Method. J. M. KOLTHOFF (*Zeitsch. anal. Chem.*, 1917, **56**, 568—576).—Trustworthy results may be obtained in this method if, as recommended by Schoorl, the titration is interrupted at the first change in colour

of the indicator, the mixture then stirred thoroughly, and the titration completed. Rothmund's modification (A., 1909, ii, 932) is less trustworthy. The author finds that it is best to dilute the solution containing the chloride and an excess of silver nitrate to a definite volume, shake the mixture thoroughly, allow the precipitate to settle, and titrate an aliquot portion of the clear solution with thiocyanate. As the silver chloride absorbs about 0·7% equivalent of silver, a corresponding correction of 0·7% must be made on the quantity of chloride found. Chlorides may be detected and estimated in the presence of thiocyanates if the latter be oxidised by treatment with sodium peroxide in sulphuric acid solution (if hydrogen peroxide is used it should be tested previously for the presence of chlorides). W. P. S.

Estimation of Chlorates and Hypochlorites. E. RUPP (*Zeitsch. anal. Chem.*, 1917, **56**, 580—586).—Ten c.c. of a solution containing about 0·5% of potassium chlorate and calcium hypochlorite are placed in a stoppered litre flask, diluted to 100 c.c., 2 grams of potassium iodide are added, the mixture is acidified with dilute acetic acid, and, after five minutes, it is titrated with $N/10$-thiosulphate solution; this titration gives the quantity of hypochlorite present. Another portion of 10 c.c. of the solution is also placed in a large stoppered flask, and 1 gram of potassium bromide and 30 c.c. of concentrated hydrochloric acid are added. After fifteen minutes, the mixture is treated with 150 c.c. of 1% potassium iodide solution, shaken, and titrated with $N/10$-thiosulphate solution. The difference between the two titrations corresponds with the amount of chlorate in the solution. W. P. S.

Action of Sodium Sulphide on Iodine and the Use of the Reaction in Analysis. JOSEF EHRLICH (*Zeitsch. anal. Chem.*, 1918, **57**, 21—22).—Pure sodium sulphide solution reacts with free iodine to form sodium iodide; sulphur is liberated at the same time, but re-dissolves in the excess of sodium sulphide added. The iodine in an iodide solution also containing other substances may be estimated by liberating the iodine with potassium permanganate, adding an excess of sodium sulphide, separating the manganese sulphide, etc., by filtration, removing the excess of sulphide in the filtrate by treatment with zinc sulphate, and then precipitating the iodine as silver iodide. W. P. S.

Estimation of Hypobromite and Bromate, or Hypoiodite and Iodate, in Mixtures of the Same. E. RUPP (*Zeitsch. anal. Chem.*, 1918, **57**, 16—19).—The method is based on the reaction between hypobromites or hypoiodites and hydrogen peroxide, according to the equation $NaBrO + H_2O_2 = NaBr + H_2O + O_2$. The solution containing hypobromite and bromate is treated with a mixture of hydrogen peroxide and sodium hydroxide solution, the excess of the hydrogen peroxide is then removed by boiling, potassium iodide and sulphuric acid are added, and the iodine liberated by the bromate is titrated with thiosulphate solu-

tion. Another portion of the solution is treated directly with potassium iodide and sulphuric acid and titrated with thiosulphate solution. This titration is a measure of the hypobromite and bromate together, and the quantity of hypobromite present is obtained from the difference in the two titrations. A mixture of hypoiodite and iodate is analysed in the same way.   W. P. S.

Estimation of Iodates in the Presence of Bromates.

E. Rupp (*Zeitsch. anal. Chem.*, 1918, **57**, 19—21).—Bromates, when treated with dilute hydrochloric acid, are decomposed gradually with the formation of hydrobromic and hypochlorous acids, whilst iodates are not affected by this treatment. To estimate the two salts when contained in the same solution, a portion of the latter is treated with potassium iodide and sulphuric acid and titrated, after a few minutes, with thiosulphate solution. Another portion of the solution is diluted with water to 50 c.c., 20 c.c. of 12·5% hydrochloric acid are added, and, after one hour, the mixture is treated with 25 c.c. of 3% hydrogen peroxide solution and 15 c.c. of 15% sodium hydroxide solution, boiled for ten minutes, cooled, and titrated with thiosulphate solution after the addition of potassium iodide and sulphuric acid. The first titration gives the quantities of bromate and iodate together, and the difference between the two titrations corresponds with the quantity of bromate present.   W. P. S.

Estimation of Sulphur in Pyrites.

Z. Karaoglanow [with P. and M. Dimitrow] (*Zeitsch. anal. Chem.*, 1917, **56**, 561—568). —After the sulphur has been oxidised to sulphuric acid by heating with a mixture of nitric and hydrochloric acids, or by fusion with sodium carbonate and potassium nitrate, the sulphuric acid may be precipitated directly from the hydrochloric acid solution obtained after separating the silica, previous removal of the iron being unnecessary if the precipitation is carried out under the following conditions. The solution (from 0·5 gram of pyrites), which should contain from 30 to 50 c.c. of 6N-hydrochloric acid (free), is diluted to 700 c.c., heated to boiling, and 40 c.c. of hot 10% barium chloride solution diluted previously with 100 c.c. of hot water are added gradually while the mixture is stirred. The precipitated barium sulphate is collected after fifteen hours, washed first with water containing hydrochloric acid and barium chloride, then with hot water, dried, ignited, and weighed.   W. P. S.

Gravimetric Estimation of Sulphuric Acid and Barium as Barium Sulphate. II.

Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1917, **56**, 487—498. Compare this vol., ii, 47).—In the estimation of barium, the presence of nitric acid or a large quantity of hydrochloric acid causes the results obtained to be too low; potassium salts and ferric chloride have the opposite effect. Under equal conditions, the errors in the gravimetric estimation of barium are less than in the estimation of sulphuric acid   W. P. S.

Detection of Selenium in Sulphuric Acid. LUCIANO P. J. PALET (*Anal. Soc. Quim. Argentina*, 1917, **5**, 121—123).— Sulphuric acid containing selenium gives an intense violet coloration with aspidospermine. The pure acid does not give this reaction, but in presence of an oxidiser, such as potassium chlorate or lead peroxide, it develops a rose-red coloration. [Compare *Ind.*, 147A.] A. J. W.

Estimation of Nitrogen in Calcium Cyanamide. (MLLE.) BRONISLAVA TURKUS (*Ann. Chim. anal.*, 1918, **23**, 3—5).—In the estimation of nitrogen in cyanamide by Kjeldahl's method, only thirty minutes' digestion with sulphuric acid is required for the complete decomposition of the cyanamide if the sulphuric acid used is diluted previously with one-fourth of its volume of water; for 1 gram of the sample, 40 c.c. of concentrated sulphuric acid mixed with 10 c.c. of water are required. The digestion must be prolonged for more than thirty minutes if the acid used is weaker or stronger than the concentration given. W. P. S.

The Microchemical Estimation of Nitrogen. B. SJOLLEMA and C. W. G. HESSERSCHY (*Biochem. Zeitsch.*, 1917, **84**, 359—370). —A critical examination of the methods of Bang and of Folin and Denis, with some suggested minor alterations of the details.
S. B. S.

Simple Rapid Method of Estimating the Filtrate Nitrogen in Small Quantities of Blood and of other Body Fluids. R. DONALD (*Quart. J. Med.*, 1917, **11**, 19—29).—One c.c. of blood is mixed with 1 c.c. of a saturated solution of sodium chloride in a mixture of nine parts of 6% sulphuric acid and one part of 6% phosphoric acid. It is centrifugalised, and 1 c.c. of the clear liquid is then transferred to a second centrifugal tube, mixed with 0·1 c.c. of 10% phosphomolybdic acid, and again centrifugalised. Of the final clear, protein-free liquid, 1 c.c. is injected into a solution of sodium hypobromite contained in a Doremus ureometer, and the nitrogen evolved is transferred to a calibrated narrow measuring tube and its volume measured. Attention is directed to the necessity of rapping the ureometer prior to the removal of the nitrogen to the measuring tube in order to liberate a considerable proportion of the gas, which otherwise remains in the gas-supersaturated hypobromite solution. The result is obtained in about forty-five minutes from the commencement of the operations, and is stated to be sufficiently accurate for clinical purposes.
H. W. B.

Estimation of Amino-acid Nitrogen in the Blood. SEIZABURO OKADA (*J. Biol. Chem.*, 1918, **33**, 325—331).—The chief point in the new method is the removal of the proteins of the blood by heating with dilute acetic acid, the last traces of protein being removed by shaking with kaolin. The use of alcohol as a precipitant is shown to be undesirable (compare Bock. A.. 1917, ii, 159). H W. B.

The Estimation of Residual Nitrogen of the Blood.
B. SJOLLEMA and C. W. G. HESSERSCHY (*Biochem. Zeitsch.*, 1917, **84**, 371—377).—Different results are obtained according to whether phosphomolybdic acid, metaphosphoric acid, or trichloroacetic acid is used as precipitant of the proteins.   S. B. S.

Still-head for Use in the Distillation of Ammonia.
A. HUTIN (*Ann. Chim. anal.*, 1917, **22**, 242—244).—The apparatus consists of a bulb with a lower tube which enters the neck of the distillation flask, and an upper tube connected with a receiver; this upper tube extends into the bulb, the portion inside the bulb being constricted and bent upwards. If desired, a wide tube filled with glass beads may be placed between the lower tube of the still-head and the distillation flask. The whole apparatus is made of sheet tin, and its purpose is to prevent any spray from the distillation flask passing over into the receiver.   W. P. S.

Use of Diphenylamine-Sulphuric Acid for Colorimetric Estimations.
J. TILLMANS (*Zeitsch. anal. Chem.*, 1917, **56**, 509—511).—A reply to L. Smith (A., 1917, ii, 217). The use of diphenylamine for the colorimetric estimation of nitric acid is trustworthy if the test solution and the standards are treated in exactly the same way, particularly as regards shaking or stirring.
                                                                W. P. S.

Estimation of Phosphorous, Hypophosphoric, and Phosphoric Acids in Mixtures.
R. G. VAN NAME and WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **45**, 91—102).—The estimation of phosphorous acid in presence of hypophosphoric and phosphoric acids may be effected by the absorption of iodine in presence of disodium hydrogen phosphate.

The same method may be used for the estimation of hypophosphoric acid if this is hydrolysed in presence of hydrochloric acid as catalyst, producing thereby equimolecular quantities of phosphorous and phosphoric acids in accordance with the equation $H_4P_2O_6 + H_2O = H_3PO_3 + H_3PO_4$.

A mixture of phosphorous, hypophosphoric, and phosphoric acids may be analysed by estimating the phosphorous acid before and after hydrolysis by the iodometric method, and also determining the total phosphoric acid in the solution after oxidation. [See, further, *Ind.*, 147A.]   H. M. D.

The Precipitation of Phosphoric Acid in the State of Ammonium Phosphomolybdate. Estimation of Phosphoric Acid by a Simple Azotometric Method.
J. CLARENS (*Compt. rend.*, 1918, **166**, 259—262).—If the phosphate is precipitated by ammonium molybdate in the presence of sufficient ammonium nitrate, the resultant precipitate contains phosphoric acid and ammonia in the proportions requisite to form triammonium phosphate. The proportions to use should be 0·1 gram of phosphoric anhydride and 100 c.c. of ammonium molybdate containing 15—20 grams of ammonium nitrate. The precipitate is washed with dis-

tilled water, and the ammonia present estimated by one of the usual methods, such as distillation with potassium hydroxide.

W. G.

Estimation of Phosphoric Acid. A Modification of the Citrate Method. J. GROSSFELD (*Zeitsch. anal. Chem.*, 1918, **57**, 28—33).—To avoid the intermediate precipitation of phosphoric acid by molybdic acid, the author proposes a method for the analysis of fertilisers, ashes, etc., in which the calcium is precipitated as oxalate from an acetic acid solution, and, after the removal of the calcium oxalate, the phosphoric acid is precipitated in the usual way as ammonium magnesium phosphate, citric acid being added to prevent precipitation of iron and aluminium. The hydrochloric acid solution (or other solution) of the substance under examination is treated with a few drops of methyl-orange solution and an excess of ammonium oxalate solution, and saturated ammonium acetate or sodium acetate solution is added until the colour of the indicator changes from red to yellow; the mixture is then diluted to 100 c.c., mixed, and filtered through a kieselguhr filter. An aliquot portion of the filtrate is mixed with 5 c.c. of 20% citric acid solution and the phosphoric acid precipitated with magnesia mixture. W. P. S.

Estimation of Phosphoric Acid, particularly in Superphosphate. G. VORTMANN (*Zeitsch. anal. Chem.*, 1917, **56**, 465—487).—For the direct estimation of phosphoric acid in superphosphate, the most trustworthy method consists in precipitation as ammonium magnesium phosphate after the calcium has been removed as oxalate and the iron as sulphide; the presence of ammonium oxalate, ammonium molybdate, and ammonium sulphide does not interfere with the precipitation. If aluminium salts are present, the quantity of magnesia mixture used should be increased. When the phosphoric acid is precipitated with molybdic acid solution before it is converted into ammonium magnesium phosphate, the precipitation may be made equally well from a nitric, hydrochloric, or sulphuric acid solution. Molybdic acid solution containing pyridine is a very sensitive reagent for the detection of traces of phosphoric acid; it will detect 0.01 mg. of P_2O_5 in 10 c.c. of solution, whilst the limit for molybdic acid containing nitric acid is about 0.1 mg. of P_2O_5 in 10 c.c. The phosphoric acid in superphosphate can also be precipitated as a basic mercury compound by means of yellow mercuric oxide; this compound is then decomposed with sodium sulphide, and the phosphoric acid precipitated as ammonium magnesium phosphate. Precipitation as calcium triphosphate is untrustworthy. [See also *Ind.*, 160A.]

W. P. S.

Use of Textile Fibres in Microscopic Qualitative Chemical Analysis. II. Detection of Boron by means of Turmeric Viscose Silk Fibres. III. Detection of the Heavy Metals by means of Zinc Sulphide Wool Fibres. E. M. CHAMOT and H. I. COLE (*J. Ind. Eng. Chem.*, 1918, **10**, 48—50. Compare A., 1917, ii, 576).—Viscose silk fibres dyed with turmeric are

useful for the detection of very small quantities of boric acid; a reaction may be obtained with one drop of solution containing 0·000025 mg. of boron. Wool fibres, free from fat and treated with sodium sulphide and zinc acetate, are suitable for the detection of heavy metals, the coloration obtained indicating the metal present. [See, further, *Ind.*, 75A.]   W. P. S.

Rapid Organic Combustion. P. A. LEVENE and F. W. BIEBER (*J. Amer. Chem. Soc.*, 1918, **40**, 460—462).—The procedure adopted in the authors' laboratory is fully described, with diagrams. Cerium dioxide is used as a catalyst, and from the first weighings to the final ones, the combustion requires only about forty-five minutes.   J. C. W.

Micro-analysis of Organic Substances. J. V. DUBSKY (*Ber.*, 1917, **50**, 1709—1713).—An account of recent experiences and improvements of micro-methods of combustion, made in the university laboratory at Zurich, where all analyses are now performed with small quantities of material. For the combustion of halogeno-nitro-compounds, the tube contains a 5 cm. layer of pieces of fine silver wire, then a 16 cm. layer of a mixture of copper oxide and lead chromate, then another short layer of silver, and finally the boat. The preliminary decomposition is carried out with the oxygen supply cut off, and if the compound is very poor in hydrogen (for example, trichlorodinitrobenzene) it is found best to adopt Benedict's method (A., 1900, ii, 439) and place before the boat another boat containing a weighed amount of pure benzoic acid, naphthalene, or sugar, in order to reduce some of the copper oxide. [See also *Ind.*, April.]   J. C. W.

Electrical Combustion Furnaces for Micro-analyses. J. V. DUBSKY (*Ber.*, 1917, **50**, 1713—1717).—A description of a platinum resistance and a chromium–nickel resistance furnace designed at the author's instigation for use with silica combustion tubes. [See *Ind.*, April.]   J. C. W.

The Eggertz Test for Combined Carbon in Steel. J. H. WHITELEY (*Iron Steel Inst. Carnegie Schol. Mem.*, 1917, **8**, 1—101).—Small quantities of carbon dioxide may be accurately estimated by absorbing in an ammoniacal solution of barium chloride (McFarlane and Gregory, A., 1906, ii, 802), and an apparatus is described by the use of which the carbon in steel may be estimated by wet combustion or the weight of carbon dioxide evolved during the Eggertz colour test may be determined. This gas is given off, at a decreasing rate, during several hours' heating, and the quantity obtained in a given time is closely proportional to the carbon content of the steel, irrespective of its heat treatment, the only exceptions being austenitic steels. The other volatile products of the reaction include hydrogen cyanide and hydrocarbons, the 'missing' carbon remaining in solution, as shown by oxidation with permanganate. A 1% carbon steel yields, in the

first ten minutes' boiling with nitric acid, 22% of its carbon as carbon dioxide, 5—10% as hydrogen cyanide, and 2—3% as hydrocarbons. The colouring matter of the brown solution is colloidal. When steel is dissolved in nitric acid kept cool by water, a black precipitate forms in all cases in which carbide particles are visible in the section etched with sodium picrate. This precipitate becomes brown later, especially on warming, and later this changes to a brown solution. The particles first formed have the form of the carbide. Quenched steels yield the solution directly. On dialysis, a substance passes through the membrane, which has an orange colour in concentrated solution, but becomes green on dilution. The colour is not merely that of the organic substances present, but depends on the reaction of these with iron. With further heating, the green substance changes to a colourless or only slightly coloured substance. The proportions of the coloured products depend on the electro-chemical conditions of solution, and cold-worked steels give a deeper colour. The tints given by different steels are more easily matched if sulphuric acid be added. For 0·5 gram of steel, 10 c.c. of nitric acid (1·2) are used, and, after boiling for fifteen minutes, 15 c.c. of sulphuric acid (1 : 3 by volume) are added. [See, further, *Ind.*, 1917, 1097.] C. H. D.

Gravimetric Estimation of Potassium by Sodium Cobaltinitrite. C. V. GAROLA and V. BRAUN (*Ann. Falsif.*, 1917, **10,** 572—575).—The reagent used consists of 28·6 grams of cobalt nitrate and 50 c.c. of glacial acetic acid dissolved in 500 c.c. of water, and 180 grams of sodium nitrite also dissolved in 500 c.c. of water; these two solutions are mixed twenty-four hours before use and then filtered. The mixed reagent keeps for a few days only. Twenty-five c.c. of the potassium salt solution (containing about 0·250 gram of potassium chloride and free from other bases except sodium) are treated in a stoppered flask with 25 c.c. of the reagent, and, after about eighteen hours, the precipitate is collected on an asbestos filter, washed with 10% acetic acid, then once with 95% alcohol, dried at 100°, and weighed. The precipitate contains 20·74% of K_2O. The method is trustworthy for the estimation of potassium in fertilisers, soils, wines, etc. Ammonium salts should be removed previously by ignition and other bases by treatment with sodium carbonate and filtration. [See also *Ind.*, 168A.]
W. P. S.

Estimation of Potassium and Sodium as Chlorides through the use of the Refractometer. B. A. SHIPPY and G. H. BURROWS (*J. Amer. Chem. Soc.*, 1918, **40**, 185—187).—The refractive index at 25° of a 20% sodium chloride solution is 1·36829, whilst that of a 20% potassium chloride solution is 1·35992. If, therefore, the refractive index of a 20% solution of the mixed chlorides be determined, the approximate quantities of the two salts can be found by a simple calculation. [See also *Ind.*, 168A.]
W. P. S.

A Proximate Method for the Estimation of Rubidium and Cæsium in Plant Ash. W. O. ROBINSON (*J. Ind. Eng. Chem.*, 1918, **10**, 50—51).—After removal of phosphoric acid, calcium, magnesium, etc., the mixed alkali chlorides are fractionally precipitated with platinum chloride. The potassium, rubidium, and cæsium platinichlorides are collected, reduced in hydrogen and the resulting chlorides treated with concentrated hydrochloric acid. The solution thus obtained, containing all of the rubidium and cæsium chlorides and a large amount of potassium chloride, is then compared spectroscopically with standard solutions containing known amounts of rubidium, cæsium, and potassium chlorides, and prepared under the conditions given. [See, further, *Ind.*, 76A.]   W. P. S.

Colloido-chemical Methods for Estimating the Hardness of Water. L. BERCZELLER (*Biochem. Zeitsch.*, 1917, **84**, 149—155).—The surface tension of soap solutions is diminished considerably by addition of small amounts of alkali hydroxides, but the addition to such alkaline solutions of small amounts of calcium or magnesium salts increases the surface tension. These facts might form a basis for a method for determining the hardness of water.

S. B. S.

Estimation of Zinc by Schaffner's Method. V. HASSREIDTER (*Zeitsch. anal. Chem.*, 1917, **56**, 506—509. Compare A., 1917, ii, 509).—In any of the modifications of this method, the precipitation of the iron (whether it be a single, double, or treble precipitation), should be carried out under conditions which will minimise the retention of zinc. It is advisable to make a comparison precipitation at the same time, using a definite quantity of iron and zinc. The iron precipitate should be tested for the presence of zinc. [See also *Ind.*, 168A.]   W. P. S.

Estimation of Zinc on Galvanised Iron. O. BAUER (*Stahl u. Eisen*, 1915, 734; from *Ann. Chim. anal.*, 1918, **23**, 21).—A measured and weighed piece of the metallic sheet is treated with a solution containing 2 grams of sulphuric acid and 2 grams of arsenic trioxide per litre; this solution dissolves the zinc readily, but does not attack the iron. When evolution of hydrogen ceases, the remaining sheet of iron is removed from the solution, washed, dried, and re-weighed. This method can be used only with galvanised iron prepared electrolytically; when it is made by the hot dipping process, an iron–zinc alloy is formed between the layers of iron and zinc, and this alloy dissolves in the reagent. The presence of iron in the solution indicates that the galvanised iron had been made by the hot process.   W. P. S.

Estimation of Lead as Phosphate and its Separation from Antimony. G. VORTMANN and A. BADER (*Zeitsch. anal. Chem.*, 1917, **56**, 577—580).—The solution, containing about 0·5 gram of lead nitrate, is treated with 5 grams of tartaric acid, then rendered

slightly ammoniacal, heated at 80°, and 100 c.c. of 10% ammonium phosphate solution are added. The mixture is kept at 70—80° for sixteen hours, then cooled, the precipitate collected, washed with dilute ammonium nitrate solution, dried, ignited at a low temperature, and weighed. If antimony is present, the quantity of tartaric acid used is correspondingly increased; antimony is not precipitated under these conditions, and may be estimated as sulphide in the filtrate from the lead phosphate precipitate. The method yields trustworthy results and is useful for the analysis of "hardened" lead. W. P. S.

Separation of the Copper Group from the Arsenic Group, with Especial Reference to the Identification of Arsenic. M. CANNON SNEED (*J. Amer. Chem. Soc.*, 1918, **40**, 187—191).— The method depends on the solubility of mercury, arsenic, antimony, and tin sulphides in a solution prepared by saturating a 12% sodium hydroxide solution with hydrogen sulphide and adding to each litre 400 c.c. of 40% sodium hydroxide solution. Lead, bismuth, copper, and cadmium sulphides remain insoluble. The solution containing the soluble sulphides is treated with ammonium carbonate to precipitate the mercury; arsenic, antimony, and tin sulphides are precipitated by hydrochloric acid, and the antimony and tin sulphides are separated by solution in warm concentrated hydrochloric acid. The arsenic sulphide is dissolved in ammonia, oxidised with nitric acid, and the solution at 80° treated with an excess of ammonium molybdate. The latter yields a yellow precipitate with the arsenic, and will detect as little as 1 part of arsenic in 225,000 parts of water. [See, further, *Ind.*, April.] W. P. S.

New Methods for the Estimation of Copper, Zinc, Cadmium, Nickel, and Cobalt. ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 245—251).—To a solution containing any one of these metals, sodium carbonate in slight excess is added in the cold until it is just alkaline. The precipitate formed is then redissolved by the addition of just sufficient ammonium hydroxide, or, in some cases, ammonium carbonate, and the liquid is boiled, usually for five minutes, until precipitation is complete. The precipitate is washed, dried and ignited, and weighed as the oxide, or reduced and weighed as the metal. If the amount of precipitate obtained is very small, it is dissolved in a little nitric acid, the solution evaporated to dryness with a little sulphuric acid, and the metal weighed in the form of its anhydrous sulphate. In every case, it is essential to ensure the absence of all ammonium salts prior to the precipitation with sodium carbonate. W. G.

New Separations of the Five Metals of the Group Soluble in Ammonia. ADOLPHE CARNOT (*Compt. rend.*, 1918, **166**, 329—333. Compare preceding abstract).—If copper and zinc are present together in solution, they are precipitated and weighed as their combined oxides (*loc. cit.*), and these are then heated in a current of hydrogen. The zinc volatilises as formed, and the

residual copper is weighed. With a mixture containing copper, nickel, and zinc, the copper is first precipitated from the boiling acid solution by the addition of sodium thiosulphate and weighed as its sulphide. From the filtrate, the nickel and zinc are precipitated and weighed as the mixed oxides, these being then reduced in hydrogen and the nickel weighed. For an alloy of zinc and cadmium, the metal is dissolved in nitric acid and. the solution evaporated nearly to dryness, and then diluted to 150—200 c.c. Sodium carbonate is added until the liquid is alkaline, and then ammonium sesquicarbonate and a little ammonia, the liquid being heated to just below 100° until it no longer smells of ammonia. The cadmium carbonate is washed by decantation with ammonium carbonate solution until free from zinc, and then ignited and weighed as cadmium oxide. The zinc is estimated in the filtrate by Meunier's method (compare A., 1897, ii, 464).

Cobalt may be separated from nickel, when in solution with it, by precipitation with ammonium sulphide in the presence of an alkali oxalate. The nickel passes through in solution on filtering, and is precipitated from the filtrate as nickel sulphide by boiling it with acetic acid. This method also applies to the separation of copper and nickel if an alkali sulphide is used in place of ammonium sulphide.

By a combination of these methods, the five metals if present in solution together may be separated and estimated.   W. G.

The Examination of Mercury Fulminate and the Analysis of Mixtures for Percussion Caps. PAUL NICOLARDOT and JEAN BOUDET (*Compt. rend.*, 1918, **166**, 258—259).—Free mercury may be detected in the fulminate by shaking 1 gram of the latter with 100 c.c. of a 5% solution of ammonium thiosulphate. All the fulminate dissolves and leaves the mercury as a grey powder or in metallic globules, which can, if necessary, be weighed.

For the examination of detonating mixtures, the percussion caps are treated first in the cold for two hours, and then at 60° for one hour with yellow ammonium sulphide. The mercury fulminate is converted into mercury sulphide, which is filtered off along with any powdered glass present. To the filtrate, ammonium sulphite is added, and the antimony sulphide which separates is collected and weighed. In the filtrate, the alkali metals are estimated in the usual way. Any chlorate or nitrate in the mixture is extracted with cold water and estimated in the usual manner. Any copper present, owing to the attack of the metal of the caps, will come down with the antimony sulphide, and may be estimated electrolytically after calcining the sulphides and extracting them with nitric acid.   W. G.

Estimation of Manganese in Steel in the Presence of Chromium and Vanadium by Electrometric Titration. G. L. KELLEY, M. G. SPENCER, C. B. ILLINGWORTH, and T. GRAY (*J. Ind. Eng. Chem.*, 1918, **10**, 19—23).—The manganese is

oxidised to permanganate by sodium bismuthate or ammonium persulphate, and the permanganate then titrated with mercurous nitrate solution. The solution to be titrated should contain about 50 c.c. of sulphuric acid (D 1·58) per 200 c.c. of water, and the temperature should be 20°. The end-point of the titration, as observed on the electrometric apparatus, is sharp and is not affected by the presence of chromates or vanadates. [See, further, *Ind.*, 92A.] W. P. S.

Analysis of Tin Ores. T. F. GOLICK (*Eng. Min. J.*, 1916, 827; from *Ann. Chim. anal.*, 1917, **22**, 248).—The ore is fused with a mixture of potassium carbonate and sulphur, the mass, when cold, is extracted with hot water, and the solution filtered. The filtrate is then evaporated with the addition of sulphuric acid and heated until sulphuric acid fumes are evolved, the residue treated with hydrochloric acid and hydrogen peroxide to insure complete conversion of the tin into stannic chloride, and the tin precipitated as sulphide. After the precipitated sulphide has been collected and washed, it is treated with a known quantity of potassium iodate in the presence of concentrated hydrochloric acid, and the excess is titrated with potassium iodide solution; the reaction proceeds according to the equation: $SnS_2 + KIO_3 + 6HCl = SnCl_4 + S_2 + KCl + ICl + 3H_2O$. W. P. S.

Detection of Small Quantities of Vanadium in Water. VICTOR L. MEAURIO (*Anal. Soc. Quim. Argentina*, 1917, **5**, 185—189).—A solution of 0·2 gram of diphenylamine in 100 c.c. of water in presence of hydrochloric acid gives a violet coloration with aqueous solutions of vanadium compounds. The coloration is unaffected by the presence of nitrates, iron, or titanates, and the test will detect the presence of vanadates in solutions of 0·0002% strength. [Compare *Ind.*, April.] A. J. W.

The Estimation of Vanadium in the Presence of Molybdenum by means of Titanous Chloride. A. TRAVERS (*Compt. rend.*, 1918, **166**, 289—290. Compare A., 1917, ii, 545).—In using the method previously described (*loc. cit.*), it is now noted that if the indicator, potassium thiocyanate, is added before the titanous chloride, the vanadic acid is reduced first, and when this action is complete, the molybdic acid is reduced. Thus vanadium and molybdenum in steels may be estimated by carrying out the method for the two together, as already described (*loc. cit.*), and then in another portion estimating the vanadium alone by adding the thiocyanate first and running in the titanous chloride from a burette until an end-point is reached. W. G.

Antimony Dioxide. JULIUS VON SZILÀGYI (*Zeitsch. anal. Chem.*, 1918, **57**, 23—28).—Antimony dioxide may be prepared by heating the pentoxide at bright redness or by oxidising antimony with concentrated nitric acid and heating the resulting oxide at dull redness until constant in weight. When heated with concentrated

hydrochloric acid and potassium iodide, antimony dioxide liberates iodine; the reaction proceeds according to the equation: $2SbO_2 + 6HCl + 2HI = 2SbCl_3 + 4H_2O + I_2$. The iodine may be separated by distilling the mixture; if the distillate is collected in a receiver containing potassium iodide solution, titration with thiosulphate solution will give the quantity of antimony dioxide present. Meta-stannic acid does not liberate iodine from potassium iodide under the above conditions, but the reaction is of little practical use for the estimation of antimony in the presence of tin, since alloys of these two metals usually contain other metals which interfere.

W. P. S.

Colorimetric Estimation of Bismuth (in Copper). H. A. B. MOTHERWELL (*Eng. and Min. J.*, 1917, **104**, 1091—1092; from *J. Soc. Chem. Ind.*, 1918, **37**, 92A).—The copper is dissolved in nitric acid, and the cold diluted solution treated with sodium carbonate until a small quantity of the copper is precipitated; this precipitate will also contain all the bismuth. After six hours, the precipitate is collected, dissolved in hydrochloric acid, the copper and bismuth are separated as sulphides, and these are dissolved in nitric acid. To the solution are added 5 c.c. of lead nitrate solution (13·5 grams per litre), the mixture is nearly neutralised with ammonia, treated with an excess of ammonium carbonate, boiled, cooled, the precipitate collected and dissolved in nitric acid, and the precipitation is repeated. If much copper is still present, dilute potassium cyanide solution must be added until the coloration has nearly disappeared, and the precipitate is then washed until free from copper. The precipitate is dissolved in a small quantity of nitric acid, the solution evaporated, the residue dissolved in three drops of nitric acid and 5 c.c. of water, the solution diluted to 25 c.c., and made up to 50 c.c. with 1·7% potassium iodide solution. The coloration obtained is at once compared with that given by a known amount of bismuth under the same conditions and in the presence of 5 c.c. of the lead nitrate solution.

W. P. S.

The Estimation of Humus by means of a Simplified Procedure of Elementary Analysis. A. JAKOBSEN (*Zhur. Optyn. Agron.*, 1916, **17**, 93—98; *Expt. Stat. Rec.*, **36**, 614; from *Physiol. Abstr.*, 1918, **2**, 629—630).—The humus in soils is estimated by a combustion method, using platinised asbestos as a catalyst. From 1 to 25 grams of material may be used, and the oxidation is complete in thirty minutes. It is claimed that the method is as satisfactory as the more complex one of Gustavson.

W. G.

Determination of the Concentration of the Hydrogen Ions in Acid Liquids. Application to Wines. MARCEL DUBOUX (*J. Chim. Phys.*, 1917, **15**, 473—501).—Two methods are described, namely, a graphic method and a method of calculation, the latter giving the more precise results.

In the first method, a neutralisation curve is drawn, plotting the conductivity of the solution against the volume of standard alkali added, the wine being previously diluted with water in the proportion of 1 : 4 or 3 : 97 by volume, according as the amount of alkali required to neutralise 1 litre of it, as determined volumetrically, is less or greater than 110 c.c. N-sodium hydroxide. The tangent to the curve at the neutralisation point is drawn, and the distance x from its point of intersection with the ordinate axis (conductivity) to the curve along the axis is measured. Then $[\text{H}^{\cdot}] = x/0\cdot291$, or $x/0\cdot157$, according to the dilution used.

In the method of calculation, it is necessary to determine (1) the volume of N-sodium hydroxide required to neutralise 5—5·2 c.c. of the wine; (2) the percentage of alcohol by volume in a mixture of 1 c.c. of wine to 4 c.c. of water; (3) the specific conductivity of the wine before and after the addition of the volume of alkali as determined in (1). Formulæ are given for the calculation of the hydrogen ion concentration from these data. W. G.

Volumetric Estimation of Formic Acid in the Presence of Hydroxides, Carbonates, Oxalates, and Acetates. F. TSIRO PINAS (*J. Ind. Eng. Chem.*, 1917, **9**, 1110—1111).—The solution, containing from 2·5 to 5 grams of formic acid, together with carbonates, oxalates, and acetates, is boiled for a few minutes, rendered alkaline with sodium hydroxide, and treated with a quantity of calcium chloride sufficient to precipitate the carbonates and oxalates. The mixture is filtered, the filtrate diluted to 250 c.c., and 50 c.c. are acidified with sulphuric acid and boiled in a flask with 400 c.c. of chromic acid solution (50 grams of sodium dichromate, 80 c.c. of concentrated sulphuric acid, and 500 c.c. of water) for fifteen minutes, the flask being connected, through a reflux apparatus, with a gas-measuring tube filled with water. When carbon dioxide ceases to collect in the measuring tube, the volume of the gas is observed, and its weight calculated into formic acid. Acetates, if present, do not interfere, as they are not oxidised by chromic acid. With pure sodium formate, the method yields 99·6% of the formic acid present. W. P. S.

Estimation of Acetic, Propionic, and Butyric Acids. R. D. CROWELL (*J. Amer. Chem. Soc.*, 1918, **40**, 453—460).— Various principles underlying possible methods for separating the lower aliphatic acids are discussed, and a procedure is described which depends essentially on the fact that most of the butyric acid and some propionic acid can be extracted by means of light petroleum (b. p. 150—300°) after saturating the solution under examination with calcium chloride and a little potassium chloride. The total acidity and weight of sodium salts, dried at 200°, are first determined, and then the acidity and salt weight of the light petroleum extract. The first salt weight minus the sodium acetate equivalent gives the total weight of –CH₂ groups, and the second minus the sodium propionate equivalent gives the weight of –CH₂ groups present as butyric acid. A correction for the solubility of

butyric acid in the calcium chloride solution, etc., also requires to be made. [See, further, *Ind.*, April.]   J. C. W.

Detection and Estimation of Butyric Acid. G. Denigès (*Ann. Chim. anal.*, 1918, **23**, 27—31).—Five c.c. of a butyric acid solution are mixed with 5 c.c. of hydrogen peroxide solution (0·01 vol. for each 0·01 gram of butyric acid per litre) and 1 c.c. of ammonium ferrous sulphate solution (5 grams of ammonium ferrous sulphate and 10 c.c. of 10% sulphuric acid per 100 c.c.). The mixture is heated at 70° for five minutes, then treated with six drops of sodium hydroxide solution, cooled, filtered, and 5 c.c. of the filtrate are mixed with three drops of sodium hydroxide solution, three drops of 5% sodium nitroprusside solution, and a slight excess (0·5 c.c. or more) of acetic acid. A red coloration develops, its intensity depending on the quantity of butyric acid present. The amount of the acid in the solution may be estimated colorimetrically by comparison with standards under the same conditions. The method may be applied to the estimation of butyric acid in mixtures, organic fluids, etc., after the acid has been separated by distillation or extraction.   W. P. S.

Estimation of Lactic Acid in the Presence of other Organic Acids. P. Szeberényi (*Zeitsch. anal. Chem.*, 1917, **56**, 505—506).—Lactic acid, when heated with chromium trioxide and sulphuric acid, yields acetic acid, carbon dioxide, and water; if the oxidised mixture is then distilled, the quantity of acetic acid in the distillate is a measure of the lactic acid present. The results obtained are slightly too low, since about 3% of the lactic acid is converted directly into carbon dioxide and water. Under the above conditions, tartaric acid, malic acid, citric acid, and oxalic acid are oxidised directly to carbon dioxide. Volatile acids, alcohol, acetone, and esters must be removed previously by distillation. A small portion of the lactic acid also distils over, and this quantity may be estimated approximately from the acidity and the molecular weights of the acids in the distillate. [See also *Ind.*, 165A.]   W. P. S.

Detection and Estimation of Small Quantities of Hydrocyanic Acid. J. M. Kolthoff (*Zeitsch. anal. Chem.*, 1918, **57**, 1—15).—Of the various reactions used for the detection of hydrocyanic acid, that depending on the formation of ferrocyanide is the only one which is characteristic and trustworthy. In using this reaction for the colorimetric estimation of small quantities of hydrocyanic acid, it is important to have exactly the same quantities of reagents in both the test and comparison solutions. The thiocyanate reaction (compare A., 1916, ii, 455) may be used for the purpose if it is remembered that certain body fluids (saliva, stomach contents, etc.) may already contain thiocyanate; in such cases, the hydrocyanic acid may be separated by the aeration-distillation method. The picric acid, guaiacum, phenolphthalein, silver, and iodine–starch reactions are untrustworthy, since many

substances other than hydrocyanic acid give similar reactions. In dealing with pure hydrocyanic acid, the sensitiveness of the tests (expressed in mg. of CN per litre) is as follows: ferrocyanide, 2; thiocyanate, 0·1; picric acid, 1; guaiacum, 0·004; phenolphthalein, 0·05; silver, 0·03; iodine–starch, 0·1.   W. P. S.

Detection of Picric Acid by Ferrous Tartrate Reagent.

RUPEAU (*Ann. Chim. anal.*, 1918, **23**, 15—16).—The author claims to have been the first to use ferrous sulphate–tartaric acid solution, often called Le Mithouard's reagent, for the detection of picric acid (compare A., 1917, ii, 158).   W. P. S.

Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas–Otto Process (Picric Acid, Picrotoxin, Antipyrin).

O. TUNMANN (*Apoth. Zeit.*, 1917, **32**, 441—443, 447—448; from *Chem. Zentr.*, 1917, ii, 499—501. Compare A., 1917, ii, 551).—This is a continuation of the papers referred to. *Picric acid.*—The sublimates are homogeneous, colourless, or even yellow. Typical crystals cannot be reckoned on even after recrystallisation from water or alcohol. Hydriodic acid dissolves the sublimate at once, but no crystals are formed. Zinc chloroiodide dissolves rich sublimates only on warming; on cooling, large, yellow prisms and flat, prismatic crystals are deposited; they show strong pleochroism and extinction parallel to the long axis. Bromine–potassium bromide solution acts similarly, but the prisms are less regular and not pleochroic. On the whole, reactions like the *iso*purpuric acid reaction, the picramic acid reaction, and the dyeing of wool are most satisfactory for these microchemical purposes.

Picrotoxin.—The picrotoxin sublimes at 215—225° for the most part. The sublimate exhibits no crystals but only drops, and crystallisation could not be brought about. Zinc chloroiodide and hydriodic acid yield no reaction products. Nitric acid dissolves the sublimate, but produces no coloration. Rich sublimates yield good crystals of picrotoxin when treated with hydrochloric acid, but it is better to apply 5% ferric chloride solution for this purpose, because this distinguishes picrotoxin sublimates from those of antipyrin. The sublimate and the solution are heated under a cover glass until bubbles appear; on cooling, typical pentagonal tablets can be observed. They are colourless, the large ones polarise in variegated shades and show oblique extinction. If the sublimate under the cover glass is treated with a drop of bromine–potassium bromide solution and heated, colourless prisms of bromopicrotoxinin are formed on cooling. These crystals are monoclinic, and can also be obtained by the action of bromine water.

Antipyrin.—The residues from the ethereal extraction of the acid solution yield only traces of antipyrin, because the greater quantity of this substance is extracted only when the solution is alkaline. The sublimates at first consist of drops, which eventually form groups of radially arranged, flat, prismatic crystals, which polarise strongly. These antipyrin deposits yield deep red drops

with hydrogen iodide, shining droplets with zinc chloroiodide, and droplets also with bromine–potassium bromide solution. The colour reactions ordinarily used are evident even with the smallest quantities without the aid of a microscope. Two antipyrin reactions which yield decisive crystalline precipitates are to be found in the formation of nitrosoantipyrin and ferripyrin respectively. In the former case, the sublimate is dissolved in a drop of water and treated successively with a drop of 10% sodium nitrite solution and a drop of acetic acid. The green solution deposits doubly refractive, dichroic crystals, or, if it is heated, long, yellow prisms. The ferripyrin reaction is carried out by heating the sublimate with a drop of 5% ferric chloride solution under a cover glass until bubbles are formed; on cooling, orange-yellow crystals are deposited, mostly 30—50 μ (sometimes 80 μ) long, which show yellow shades in polarised light. The reaction distinguishes antipyrin from salipyrin. In the case of salipyrin, the sublimate consists of groups of bent needles. Addition of ferric chloride produces a violet solution which remains on heating, and no crystals are deposited unless too high a temperature has been used for the sublimation. In this case, a mixture of crystals of ferripyrin and salicylic acid may be observed.   R. V. S.

Microchemistry of some Opium Alkaloids. L. VAN ITALLIE and J. VAN TOORENBURG (*Pharm. Weekblad*, 1918, **55**, 169—178). —An account of tests applicable to the alkaloids *pseudo*-morphine, protopine, tritopine, cryptopine, laudanine, laudanidine, and laudanosine. [See, further, *Ind.*, April.]   A. J. W.

Modification of the Ehrlich Indole Reaction in Bacterial Cultures. W. NOWICKI (*Wien. klin. Woch.*, 1917, **30**, 983; from *Chem. Zentr.*, 1917, ii, 498).—The culture, which should contain 8—10 c.c. of peptone water, is treated with 1 c.c. of Ehrlich's reagent and two drops of 40% formaldehyde solution. On shaking, a reddish-violet coloration appears, and by addition of alcohol the solution may be made suitable for colorimetric examination.
R. V. S.

Analysis of Blood and Urine. O. I. LEE (*St. Luke's Hosp. Med. and Surg. Rep.*, 1917, **4**; from *Physiol. Abstr.*, 1918, **2**, 587). —A mixture, prepared by adding three parts of amyl alcohol to seven parts of phenyl ether, is advocated for the prevention of foaming in analytical work. A colorimetric method for the estimation of iron in urine is described, the iron being precipitated with ammonium persulphate and ammonia, incinerated, and the ash moistened with potassium thiocyanate. The iron content of normal urine varies from 0·06 to 0·12%.

For the estimation of chlorine in blood, the proteins are coagulated by the addition of acetic acid and heating the mixture. After filtration, potassium alum and sodium carbonate are added, and the mixture is boiled and filtered, and the yellow filtrate is titrated with standard silver nitrate until a permanent red colour is obtained.   W. G.

General and Physical Chemistry.

Determination of the Carrier in the Emission of the Continuous Spectrum by the Hydrogen Canal Rays. J. STARK, M. GÖRCKE, and M. ARNDT (*Ann. Physik*, 1917, [iv], **54**, 81—110. Compare A., 1917, ii, 281).—The conditions under which the ultra-violet continuous spectrum is emitted by hydrogen canal rays have been investigated, and an attempt is made to identify the entities which are directly responsible for this radiation.

The intensity of the continuous spectrum increases as the wave-length diminishes from λ 400 to λ 240, and the increase is particularly marked in the region from λ 280 to λ 240. The distribution of the intensity is independent of the velocity of the hydrogen canal rays.

The continuous spectrum is emitted by the hydrogen canal rays in oxygen, and the intensity of this spectrum, as well as the distribution of the intensity, are the same as for the spectrum emitted by the canal rays in hydrogen. A continuous spectrum is also emitted by nitrogen canal rays in nitrogen and by oxygen canal rays in oxygen, but for cathode falls of potential varying from 800 to 8000 volts, the intensity of this spectrum is less than one-tenth of the intensity of the continuous spectrum emitted by the hydrogen canal rays. Nitrogen canal rays in hydrogen give rise to the emission of the hydrogen series lines in considerable intensity, but there is no appreciable continuous radiation even when the cathode fall of potential reaches 8500 volts.

From these observations, the conclusion is drawn that the emission of the continuous spectrum in question is characteristic of hydrogen. The facts suggest that the radiating entity is neither the hydrogen ion nor the neutral hydrogen atom, but that the continuous spectrum is due to an intermediate type in which the hydrogen ion is combined or associated with an electron, the combination representing a transition phase in the reversible change $H + \odot \rightleftarrows H$. H. M. D.

Experimental Facts and Bohr's Theory of the Hydrogen Spectra. J. STARK (*Ann. Physik*, 1917, [iv], **54**, 111—116).—A theoretical paper in which the author discusses recent observations on the continuous ultra-violet hydrogen spectrum in relation to Bohr's theory. The experimental evidence adduced in support of the view that the entities responsible for the emission of the continuous spectrum contain a single atom of hydrogen (compare preceding abstract) is considered to prove the untenability of Bohr's theory in its present form. Bohr's model of the hydrogen molecule is also incapable of affording an account of the facts which

have led the author to the opinion that the many-lined spectrum
is attributable to diatomic combinations carrying a single positive
charge.   H. M. D.

**Measurements in the Spectrum of Molybdenum accord-
ing to International Normals.** MARTHA PUHLMANN (*Zeitsch.
wiss. Photochem.*, 1917, **17**, 97—131).—Measurements of the wave-
lengths of lines in the arc spectrum of molybdenum have been
made with the aid of a large concave grating. The results obtained
for the region λ 2420 to λ 4888 are recorded and compared with
those given by Exner and Haschek. It has been suggested by
Paulson that certain pairs of lines exhibit constant frequency
differences, but the existence of this relation is not supported by
the author's measurements.   H. M. D.

**The Arc Spectrum of Tungsten according to Inter-
national Units.** MARIA BELKE (*Zeitsch. wiss. Photochem.*, 1917, **17**,
132—142, 145—168).—Wave-length measurements of the lines in
the arc spectrum of tungsten between λ 2249 and λ 6984 are
recorded and compared with the results previously obtained by
Exner and Haschek. The existence of pairs of lines with constant
differences of frequency is not indicated by the measurements. ·
                                                           H. M. D.

Colour of Inorganic Compounds. F. RUSSELL VON BICHOWSKY
(*J. Amer. Chem. Soc.*, 1918, **40**, 500—508).—A theoretical paper
in which an attempt is made to connect the colour of inorganic
substances with the valence electrons and the stability of the
electron grouping round the positive nucleus.   H. M. D.

**The Polymorphism of certain Substances (Liquid Crys-
tals and Sphaerolites with Helicoidal Winding).** PAUL GAUBERT
(*Bull. Soc. franç. Min.*, **40**, 5; from *Chem. Zentr.*, 1917,
ii, 806—807. Compare A., 1916, ii, 604; 1917, ii, 113).—Amyl
cyanobenzylideneaminocinnamate has been found to exist in four
different crystalline modifications. The stable α-form is biaxial,
optically negative, and has a high rotatory power; it is obtained
by crystallisation of the fused substance or by evaporation of
solutions. The β- and γ-forms are sphærolitic and distinguished
by differences in rotatory power; they are obtained by the rapid
evaporation of solutions. The fourth modification is that described
by Vorländer and Huth (A., 1911, ii, 165).

Anisylideneaminoazotoluene exists in five different crystalline
forms, which are all biaxial. The stable α-form is monoclinic or
triclinic, and the other four are probably rhombic. There are
also two liquid anisotropic forms of this substance, one of which is
optically positive and the other negative.

The cholesteryl esters of low freezing point readily form liquid
crystals when their solutions are evaporated. A difference in the
tendency to form solid crystals has been observed according to the
optical character of the liquid phase.   H. M. D.

The Photolysis of Uranium Salts. E. BAUER (*Schweiz. Chem. Zeit.*, 1918, **2**, 40—41).—When light is absorbed by a solution of a uranium salt, the uranyl ion undergoes a reversible change from the "dark" condition into the "light" condition; when the reverse action takes place, the light energy absorbed is given off again in the form of fluorescence. The addition of certain substances, such as chlorine or iodine ions, ferric and vanadyl salts, vanadic acid, and quadrivalent uranium salts, extinguishes the fluorescence. The same substances also destroy the Becquerel effect. In the "light" condition, the uranium is resolved into a higher (octavalent) and a lower (tervalent) stage of valency, and the two reunite to the sexavalent form in reverting to the "dark" condition. When an inhibiting substance is added, the formation of the intermediate products is prevented, because they are immediately taken up by the substance, for example, iodine to form the sexavalent ion. Under the influence of light, uranyl formate is decomposed with liberation of carbon dioxide and hydrogen, a reaction in which the octavalent uranyl ion plays a part. The reaction dies down again through the accumulation of the sexavalent ion, which acts as an extinguisher. Another instance of photolysis is the decomposition of oxalic acid by uranyl sulphate under the action of light. In this case, the octavalent intermediate ion produces carbon dioxide and the tervalent ion carbon monoxide, whilst the sexavalent ion is reconstituted. Analogous processes of simultaneous oxidation and reduction are held to account for the photosensitising effects of other fluorescent compounds, such as eosin.   J. F. B.

The Photolysis of Uranyl Formate. E. C. HATT (*Zeitsch. physikal. Chem.*, 1918, **92**, 513—562).—The decomposition of solutions of uranyl formate under the influence of light has been further examined with a view to the determination of the influence of the concentration of the uranyl salt, the intensity of the light, and the presence of foreign substances.

The experiments with varying concentration indicate that the photolysis is retarded by the uranous salt, which is one of the products of the light reaction. For widely varying light intensities, the initial velocity of the reaction is proportional to the intensity of the light, but at later stages the velocity increases less rapidly than the intensity of the acting light. Potassium chloride, potassium iodide, ferric chloride, vanadyl sulphate, and vanadic acid retard the reaction, but potassium sulphite appears to produce no change in the velocity of the reaction. The view that uranium compounds of higher and lower valency are formed is rendered probable by the fact that the insolated solutions have an oxidising action on potassium iodide and a reducing action on potassium permanganate. In terms of the oxidation and reduction products, it is possible to explain a number of facts which have been established in this and previous investigations of the photochemical decomposition of uranyl formate (compare A., 1916, ii, 9).

A method for the estimation of uranous salts in presence of formic acid is described. The uranium solution acidified with sulphuric acid is added to a solution containing ammonium acetate and sodium phosphate placed in a cylindrical separating funnel connected below with a suction pump through a filter bottle. The funnel is provided with a Gooch filter and with an attachment by which the air in the funnel can be replaced by hydrogen. The mixture of uranyl ammonium phosphate and uranous phosphate, which is precipitated, is filtered by suction in the hydrogen atmosphere, the precipitate washed with ammonium acetate solution, and then dissolved in sulphuric acid (1 : 4), the solution thus obtained being titrated with standard permanganate. This method of estimating uranous salts has been found to give quite satisfactory results in the investigation of the insolated uranyl formate solutions.   H. M. D.

The Scattering of α-Rays as Evidence on the Parson Magneton Hypothesis. DAVID L. WEBSTER (*J. Amer. Chem. Soc.*, 1918, **40**, 375—379).—The large-angle scattering of α-rays is generally considered to prove the untenability of theories of atomic structure which postulate large diffuse spheres of positive electricity. The magneton hypothesis, put forward by Parson (*Smithsonian Miscellaneous Collections*, 1915, **65**, No. 11), postulates such a structure, but the author contends that this is not really an essential feature, and that the α-ray scattering cannot be accepted as valid evidence against the magneton theory.   H. M. D.

Absorption Laws for Röntgen Rays. R. GLOCKER (*Physikal. Zeitsch.*, 1918, **19**, 66—72).—This paper contains a discussion of the laws expressing the absorption coefficient of X-rays as a function of the wave-length and atomic number of the absorbing element, and contains tables of the various constants involved in the formulæ for ten elements and six compounds. The data are of practical and theoretical importance, but the paper cannot be suitably abstracted.   F. S.

X-Ray Spectra and the Constitution of the Atom. L. VEGARD (*Phil. Mag.*, 1918, [vi], **35**, 293—326).—An account of work previously described (compare this vol., ii, 93, 94). The periodic variation of the electric conductivity of the elements (Benedicks, *Jahrb. Radioaktiv. Elektronik*, 1916, **13**, 362) is considered to afford support for the configurations which are put forward by the author.   H. M. D.

Solubility of Pure Radium Sulphate. S. C. LIND, J. E. UNDERWOOD, and C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1918, **40**, 465—472).—If a solution containing a mixture of radium and barium salts is partly precipitated by the addition of a sulphate, the ratio of radium to barium in the precipitate is the same as in the original solution. The behaviour resembles that which is met

with in the case of the isotopic elements, and has not yet been satisfactorily explained. With the object of providing data which may serve to elucidate the nature of the phenomenon, the authors have determined the solubility of pure radium sulphate in water and in sulphuric acid solutions.

The measurements were made by dissolving the salt and also by precipitating it from solution. The mean value obtained for the solubility in water at 25° is $2 \cdot 1 \times 10^{-8}$ gram per c.c., which is about one-hundredth of the solubility of barium sulphate. The presence of sulphuric acid up to 50% has no appreciable influence on the solubility. At higher acid concentrations, the solubility increases rapidly, the data obtained showing that the solubility is more than twelve times as great in 70% acid as in 60% acid. In dilute acid solutions, the solubility increases about 50% when the temperature is raised from 25° to 35°, and the same increase is found when the temperature is raised to 45°. .The observed value of the solubility of radium sulphate is in agreement with that expected from a comparison of the solubilities of the sulphates of calcium, strontium, and barium.

The term pseudo-isotopy is given to the phenomenon which is exhibited by radium and barium sulphates. H. M. D.

Radioactivity of the Lake of Rockange. (Miss) H. J. FOLMER and A. H. BLAAUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 714—735).—A detailed account is given of the investigation of the radioactivity of samples of mud obtained by borings to different depths from the floor of the lake of Rockange (Hook of Holland). In contradiction to certain previous observations, the authors' results lead to the conclusion that the alluvial mud of the lake possesses no radioactivity of importance. The figures obtained correspond with an average value of the order of 10^{-12} gram of radium per gram. With regard to the origin of this, it is suggested that the radioactive substance in the mud is for the most part brought down by the rivers and does not come from the dunes. H. M. D.

Electrical Conductance of Solutions in Bromine. EDWARD H. DARBY (*J. Amer. Chem. Soc.*, 1918, **40**, 347—356).—Trimethylammonium chloride is readily soluble in liquid bromine, producing solutions of a yellow colour, the viscosity of which increases very rapidly with the concentration. The electrical conductivity of these solutions has been measured at 18° with results which show that the equivalent conductance of the salt increases from $0 \cdot 3186$ at $c = 0 \cdot 09076$ gram-equivalents per litre to $11 \cdot 49$ at $c = 1 \cdot 2356$. The variation of the conductance with the concentration is in agreement with the equation of Kraus and Bray. The constants have values which are comparable with those obtained for electrolytes in other solvents.

The conductance of trimethylammonium chloride is much greater than that obtained for iodine and phosphorus pentabromide,

the conductance of which in liquid bromine has been previously examined by Plotnikov and Rokotjan (A., 1913, ii, 378).

H. M. D.

The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid. J. Böeseken and H. Kalshoven (*Rec. trav. chim.*, 1918, **37**, 130—143).—In continuation of previous work (compare A., 1916, ii, 73, 209), the authors have examined the influence of glycollic, α-hydroxy-β-phenylpropionic, β-hydroxy-β-phenylpropionic, and diglycollic acids on the electrical conductivity of boric acid. Glycollic acid gave an increase in the conductivity, but the substitution of a group ·O·CH$_2$·CO$_2$H for the hydroxyl group changed the influence from positive to negative, as shown by the results with diglycollic acid. β-Hydroxy-β-phenylpropionic acid is similar to β-hydroxybutyric acid (*loc. cit.*) in its influence. The influence of α-hydroxy-β-phenylpropionic acid is positive and almost equal to that of lactic acid (*loc. cit.*).

W. G.

The Influence of some Derivatives of Nitrogen on the Electrical Conductivity of Boric Acid. J. Böeseken [with W. Sturm and G. Goettsch] (*Rec. trav. chim.*, 1918, **37**, 144—161).—The nitrogenous compounds examined were carbamide, biuret, alloxan, alloxantin, glycine, glutamic, cyanuric, and dialuric acids, dihydroquinazoline (quinoxaline), and the glycol of uric acid. The results indicate that the presence of the group ·NH·CO· has no influence on the electrical conductivity of boric acid, and that substances containing this group do not form complexes with boric acid. The results obtained with quinoxaline favour the ketonic formula $C_6H_4{<}{\substack{NH·CO \\ NH·CO}}$ for this compound. Glycine forms a complex boric acid derivative, which is, however, dissociated to a large extent, judging from the slight increase in conductivity obtained. Alloxan in aqueous solution has $K < 5 \times 10^{-9}$, and it does not form a complex with boric acid. Dialuric acid does not form a complex with boric acid. It has $K = 6 \times 10^{-5}$, the value diminishing rapidly, probably owing to oxidation. Alloxantin dissociates in aqueous solution into dialuric acid and alloxan. The glycol of uric acid slightly increases the conductivity of boric acid.

W. G.

The Influence of Boric Acid on the Electrical Conductivity of Diacetyl. J. Böeseken [with G. van der Hoek Ostende] (*Rec. trav. chim.*, 1918, **37**, 162—164).—The results obtained, although incomplete, indicate that, in concentrated solution, diacetyl is dihydrated. It has an acid reaction in aqueous solution, having $K = \pm 4 \times 10^{-7}$.

W. G.

The Influence of some Hydroxy-acids on the Electrical Conductivity of Boric Acid. J. Böeseken [with (Mlle.) J. Weisfelt, (Mlle.) J. van der Spek, Chr. van Loon, and G. Goettsch] (*Rec. trav. chim.*, 1918, **37**, 165—178. Compare preceding abstract).—Four acids were studied. α-Hydroxyoctoic acid,

like other α-hydroxy-acids, gives with boric acid a complex having a high conductivity. Glyceric acid behaves like an α-hydroxy-acid, the β-hydroxyl group having no influence on the conductivity. Dihydroxymaleic acid behaves in aqueous solution like a di-α-hydroxy-acid. Its decomposition is retarded by boric acid. With gluconic acid, the increase in the conductivity is greater than that with the other α-hydroxy-acids, the group $\vdots C(OH)\cdot CO_2H$ exerting its influence in addition to that of the four other hydroxyl groups. The opening of the lactonic ring may be followed by the regular change in the conductivity, which increases with increase in the concentration of the hydrogen ions.   W. G.

The Influence of Boric Acid on the Conductivity of some Optically Active α-Hydroxy-acids, and on that of their Racemates. J. Böeseken and L. A. van der Ent (*Rec. trav. chim.*, 1918, **37**, 179—183).—Measurements of the electrical conductivity of *r*- and *d*-amygdalic acids and *r*- and *d*-tartaric acids in the presence of boric acid show that the influence of a racemic acid on the electrical conductivity of boric acid is equal to that of its active component.   W. G.

Free Energy of Dilution of Sulphuric Acid. Merle Randall and O. E. Cushman (*J. Amer. Chem. Soc.*, 1918, **40**, 393—397).— The *E.M.F.* of cells of the type $H_2|H_2SO_4|Hg_2SO_4|Hg$ has been measured for widely varying sulphuric acid concentrations. From the results, the authors have calculated the free energy of the reaction $H_2 + Hg_2SO_4 = H_2SO_4 + 2Hg$ for acids of different concentration. In combination with previous data (compare A., 1914, ii, 521), these results also give the free energy of formation of sulphuric acid from $1N$ hydrogen and sulphate ions. The numbers obtained are tabulated.   H. M. D.

Electromotive Force and Free Energy of Dilution of Lithium Chloride in Aqueous and Alcoholic Solutions. J. N. Pearce and F. S. Mortimer (*J. Amer. Chem. Soc.*, 1918, **40**, 509—523).—The influence of the solvent on the *E.M.F.* of concentration cells has been systematically examined in experiments with solutions of lithium chloride in water and the five lowest alcohols of the series beginning with methyl alcohol. The concentration ratio was in all cases $10:1$, the absolute concentration of the stronger solution varying from $1\cdot0$ to $0\cdot05$ mol. of lithium chloride per litre.

The data recorded are those obtained with cells of two types. In the case of cells involving transference, the *E.M.F.* increases with increasing dilution in water and the three lower alcohols, but decreases with dilution in *n*-butyl and *iso*amyl alcohols. For cells arranged so that there is no transference, the observed *E.M.F.* decreases with increase in the dilution in all the solvents examined. These relations indicate that the ionisation of lithium chloride is abnormal in all these solvents.

The transport number of the lithium ion, the free energy of dilution, and the activity ratios for both the ions and the non-ionised molecules, have been calculated. The transport number increases with the dilution, whilst the free energy of dilution and the activity ratios decrease with the dilution in all the solvents examined.

An attempt is made to account for these relations by the assumption of effects due to hydration, polymerisation, and change in the dielectric capacity of the solvent.   H. M. D.

Effect of Interionic Force in Electrolytes. II. S. R. MILNER (*Phil. Mag.*, 1918, [vi], **35**, 352—364. Compare this vol., ii, 54). —The author's view, that the decrease in the molecular conductivity of electrolytes with increasing concentration is to be attributed mainly to a reduction in the mobilities of the ions, and not to a reduction in their number by their combination to form molecules, is discussed further by reference to the influence of interionic forces on the electrical conductivity and on the osmotic pressure. The theoretical investigation of this influence leads to the conclusion that a change in the concentration will produce identical variations in the conductivity and in the osmotic pressure of the free ions, that is to say, the ions which momentarily have no mutual energy with other ions.

This result, when applied to strong electrolytes, suggests that the observed changes in the conductivity and osmotic pressure of strong electrolytes with the concentration may be explained by a modification of the usual view. Interionic forces produce an increase in the frequency of occurrence of ions in an associated state, and the result of this is a reduction in the osmotic pressure of the free ions. The average mobility of an ion, taken over a period sufficiently long to include it in the free and associated state, is reduced in the same ratio, and the experimental facts are thus accounted for. If this view is correct, the ions of strong electrolytes are not associated into molecules, but pairs of oppositely charged ions which are temporarily in closest proximity will behave in a certain number of cases as if they were bound together.   H. M. D.

Alternating Current Electrolysis with Mercury Electrodes. HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 78—94). —When solutions of sodium thiosulphate are subjected to the action of an alternating current between metallic electrodes, metallic sulphides are precipitated in quantities which increase as the frequency of alternation decreases. The extent to which the electrodes are thereby corroded varies considerably with the nature of the electrode surface, and reproducible results cannot be obtained with solid metals.

When mercury electrodes are used, the changes in the surface tension give rise to a rhythmical vibration of the mercury surface which maintains the electrode in its original condition and serves

to agitate the solution in the immediate neighbourhood of the electrode. In these circumstances, reproducible results are obtained, and experiments have been made in which the same frequency of alternation was used (72000 alternations per minute), but in which changes were made in the current density, the temperature, and the concentration of the sodium thiosulphate solution.

The corrosion of the mercury electrodes increases with the current density, but not in direct proportion. The departure from proportionality is greater in the more dilute solutions. The corrosion also increases with the concentration of the thiosulphate solution, the two quantities being approximately proportional. When the concentration reaches a certain limit, a film of sulphide is formed over the mercury surface, and this greatly reduces the corrosion. The corrosion increases with rise of temperature and is increased by mechanical stirring.

Under like conditions, zinc electrodes are corroded to a much smaller extent, and although it is probable that the above factors affect the degree of corrosion, as in the case of mercury, variations in the electrode surface have a much greater influence on the actual result. H. M. D.

Thermal Leakage and Calorimeter Design. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 379—393).—The factors which play a part in the interchange of heat between a calorimeter and its environment are considered, more particularly with reference to the influence of the surrounding air. The convection currents in this air are of considerable importance in that the thermal leakage due to convection is approximately proportional to the square of the difference between the temperatures of the calorimeter and its environment. The influence of convection may be diminished by reducing the width of the air gap round the calorimeter. It is shown that gaps of from 10 to 17 mm. are most suitable for ordinary calorimeters, but larger gaps may be used in the case of large calorimeters in which smaller temperature differences are involved. Thin reflecting shields may be advantageously employed to diminish the effect of conduction. H. M. D.

Specific Heats at Low Temperatures of Sodium, Potassium, Magnesium, and Calcium Metals and of Lead Sulphide. E. D. EASTMAN and W. H. RODEBUSH (*J. Amer. Chem. Soc.*, 1918, **40**, 489—500).—On the assumption that $C_v = 3R$ is the normal higher limit for the atomic heat of an element, it would seem that the strongly electropositive metals have exceptionally large atomic heat capacities, and in order to obtain further information on this point, measurements have been made of the specific heats of sodium, potassium, magnesium, and calcium between 65° and 300° (abs.).

The method used consisted in measuring the rise of temperature

9*

produced by a known quantity of electrical energy supplied to the metal suspended in a vacuum, the change of temperature being measured by means of a carefully calibrated copper–constantan thermocouple. From the values of C_p derived from the experimental data, the values of C_v were obtained by calculation according to methods previously described.

The results obtained show that the value of C_v becomes considerably greater than $3R = 5.97$ cal. over the higher portion of the range of temperatures examined. According to Lewis and Gibson (*J. Amer. Chem. Soc.*, 1917, **39**, 2554), the curve which is obtained by plotting C_v against the logarithm of the absolute temperature is a general curve which can be made to fit the data for any one of a large number of elements by simple horizontal displacement. When the data obtained by the authors are examined in reference to this general curve, it is found that the points for sodium, magnesium, and calcium lie on the curve at lower temperatures, but are situated above it at the higher temperatures. In the case of potassium, the values of C_v lie above the curve at all temperatures examined.

The deviations from the normal curve are considered to be due to the heat capacities of the electrons, the energy absorption of which is supposed to depend on the degree of constraint to which they are subjected in the atom. This constraint diminishes with increase in the electropositive character of the metal.   H. M. D.

Boundaries of Existence of the Liquid State. W. HERZ (*Zeitsch. Elektrochem.*, 1918, **24**, 48—50).—The author has collected and tabulated the melting points and critical temperatures of a number of elements, halogen derivatives of non-metals, and some organic compounds. It is shown on comparison that in the case of metals the region of existence of the liquid decreases with increasing atomic weight in a given group of the periodic system, whilst for non-metals the region of existence increases. The same regularity holds for the halogen derivatives of the non-metals. In the case of organic compounds, the region of existence of the liquid increases with increasing molecular weight. The quotient, critical temperature/melting point, is approximately a constant for analogous groups of substances (see also Clarke, *Amer. Chem. J.*, 1896, **18**, 618).   J. F. S.

The Cryoscopic Constant of Asymmetric Heptachloropropane, $CCl_3 \cdot CCl_2 \cdot CHCl_2$. J. BÖESEKEN and J. BENEDICTUS (*Rec. trav. chim.*, 1918, **37**, 121—129).—Determinations have been made with a large number of different substances, and the results show that the heptachloropropane has a cryoscopic constant just under 120, but the solubility in it of hydroxy-compounds and acids is not very great. Acids are strongly associated in this solvent, even acids of high molecular weight, giving values equal to twice the theoretical molecular weight. Alcohols at great dilutions give almost normal molecular weights, but as the concentra-

tion increases they become associated. Hydrocarbons, chloro-compounds, amines, and esters behave normally.   W. G.

Formula giving the Saturated Vapour Pressure of a Diatomic Liquid. E. Ariès (*Compt. rend.*, 1918, **166**, 447—450. Compare this vol., ii, 61).—The author deduces the formula $\Pi = \tau^{11/4} Z/x$, where $x = [1 + \{(1 - \tau)(0\cdot86 - \tau)\}/(0\cdot353\tau^2 + 0\cdot642)]\tau_4^7$, and shows that the calculated results agree with the observed results in the cases of chlorine and carbon monoxide.   W. G.

The Anomalies which the Saturated Vapour Pressures of certain Diatomic Liquids Show. E. Ariès (*Compt. rend.*, 1918, **166**, 553—556).—The formula previously deduced from a study of chlorine and carbon monoxide (preceding abstract) applies also to hydrogen chloride and hydrogen iodide, but in the cases of oxygen, nitrogen, and nitric oxide certain anomalies occur between the values as calculated and observed.   W. G.

Thickness and Structure of the Capillary Layer of a Liquid in Contact with its Saturated Vapour. G. Bakker (*Ann. Physik*, 1917, [iv], **54**, 245—295).—By making use of the Laplacian theory of capillarity and certain thermodynamic arguments, it is shown that the number of molecules in the surface layer increases from about three at the freezing point of the liquid to a very much larger number in the neighbourhood of the critical temperature. In the case of carbon dioxide at the reduced temperature $0\cdot999°$, the number obtained lies between 300 and 1800. Thermodynamic reasoning leads to the conclusion that the thickness of the surface layer is about $1\cdot5\,\mu\mu$ at the reduced temperature $0\cdot9°$, whilst in the immediate neighbourhood of the critical temperature the thickness increases to a value represented approximately by half the wave-length of violet light. The thermodynamic method gives results which agree with those previously mentioned in so far as the number of molecules in the surface layer is concerned.

Since the number of molecules in the surface layer is very limited if the temperature is not in the neighbourhood of the critical temperature, it follows that the radius of action of the attractive forces does not extend beyond the limits of the nearest molecules. This deduction is not compatible with the assumptions involved in the original theory of Laplace.   H. M. D.

The Law of Thermochemical Processes (Summary) and of Photochemical Processes. Max Trautz (*Zeitsch. anorg Chem.*, 1918, **102**, 81—129).—According to the author's theory, reactions in gases take place only between molecules which are in an "activated" condition. A species of thermal isomerism of the molecule is assumed, and the heat energy necessary to transform the inactive into the active modification is termed the "heat of activation." In the mass-action equations developed from thermodynamic principles for reactions of the first and second orders, the

factor representing the heat of activation appears as an exponential function, and from two determinations of the velocity constant of a reaction at two different temperatures, it is possible to calculate the heat of activation. The heat of activation is a fraction of the total heat of decomposition into atoms, and this fraction can be calculated from the heat of reaction and the heat of activation. In the case of the reaction $H_2 + I_2 \rightleftharpoons 2HI$, for instance, the fraction is between one-fourth and one-third.

According to the author's theory, the time of contact between two "activated" molecules is of so short duration that the chance of simultaneous contact with a third activated atom is very small indeed. Reactions of a higher order than the second are therefore held to be impossible (compare A., 1915, ii, 338, 623, 828; 1916, ii, 304, 422).

The theory is applied to photochemical reactions, and equations are given for reactions of the first and second orders. The relation of the heat of activation to the frequency of the actinic radiation is considered, with special reference to Planck's radiation law, which is deduced in a novel manner. Just as the course of a thermochemical reaction is determined by the smallest heat of activation, to the exclusion of those reactions requiring greater heats of activation, so a photochemical reaction is determined by the smallest radiation frequency to which the substance is resonant. The relation between heat of activation and radiation frequency is expressed by an equation $q = R\beta v$, where q is the heat of activation and v is the frequency proper to the reaction. This frequency should be found in the spectrum of the reacting substances, and the possibility arises of determining heats of reaction and heats of activation spectroscopically. The theory is examined in its relation to Bunsen and Roscoe's law and the law of photochemical equivalents.   E. H. R.

The Energy Theory of Matter. H. STANLEY REDGROVE (*Chem. News*, 1918, **117**, 145—146. Compare A., 1917, ii, 411). —In a recent paper (A., 1917, ii, 164), Thornton pointed out that a constant is obtained if the molecular heats of combustion of saturated hydrocarbons are divided by the corresponding numbers of oxygen atoms which are required for the complete combustion of the hydrocarbons. An attempt has been made (Vliet, this vol., ii, 98) to utilise this relation in the calculation of the contribution of the carbon and hydrogen atoms and the valency bonds towards the heats of combustion of their compounds. It is shown that the equation thus introduced is deducible from the equations given by the author, and thus affords no additional basis for the calculations in question.

The author criticises the significance of the relation indicated by Thornton, and contends that it is not generally applicable to different groups of organic compounds.

The advantages of the author's theory as a basis for the computation of additive or partly additive properties are discussed in relation to other underlying hypotheses.   H. M. D.

Equilibria Involving Cyanogen Iodide. The Free Energy of Formation of Cyanogen. GILBERT N. LEWIS and DONALD B. KEYES (*J. Amer. Chem. Soc.*, 1918, **40**, 472—478).—The reversible reactions represented by $2CNI \rightleftharpoons (CN)_2 + I_2$ and $CNI + HI \rightleftharpoons HCN + I_2$ have been examined, and from the equilibrium data the free energy of formation of cyanogen has been calculated.

The partial pressure of iodine in the saturated cyanogen iodide vapour was determined colorimetrically by comparison of this with the vapour given off by pure solid iodine, the temperature of which was adjusted until the colours in the two comparison tubes were equal. The partial pressure obtained in this way increases from 3·42 mm. at 90·0° to 56·7 mm. at 123·0°. From these partial pressures, the equilibrium constant is calculated, and the logarithms of these numbers when plotted against the reciprocal of the absolute temperature fall very nearly on a straight line, from the slope of which the heat absorbed in the dissociation is found to be 48,000 cal. By extrapolation, the value of the equilibrium constant at 25° is obtained, and this leads to $\Delta F_{298} = 14{,}950$ for the free energy of the reaction represented by $2CNI(\text{solid}) = (CN_2) + I_2(\text{gas})$.

When a mixture of solid cyanogen iodide and iodine is treated with a dilute solution of hydriodic acid, the equilibrium represented by $CNI + H^{\cdot} + I' \rightleftharpoons HCN + I_2$ is quickly established, and methods are described by which the authors have found it possible to obtain the concentrations of the hydrogen and iodine ions and that of the hydrocyanic acid for a series of hydriodic acid solutions of varying strength. The values obtained for $K = [HCN]/[H^{\cdot}][I']$ are not very constant, but by taking the mean value $K = 13$, the free energy of the reaction $CNI(\text{solid}) + H^{\cdot} + I' = HCN(\text{gas}) + I_2(\text{solid})$ is found to be $\Delta F_{298} = -1520$.

Measurements of the partial pressure of hydrogen cyanide for aqueous solutions of varying concentration gave $P/m = 0·096$ at 25°, where P is the pressure in atmospheres and m the concentration in mols. per 1000 grams of water. From this ratio of distribution, the value $\Delta F_{298} = 1390$ is obtained for the reaction $HCN(\text{aq.}) = HCN(\text{gas})$. By combining these with values previously obtained, the free energy of formation of cyanogen iodide according to the equation $C(\text{gas}) + \frac{1}{2}N_2 + I(\text{solid}) = CNI(\text{solid})$ is found to be $\Delta F_{298} = 38{,}635$.

Combining this result with the equations for the free energy of dissociation of cyanogen iodide (see above) and the formation of iodine vapour from solid iodine, the free energy of formation of cyanogen gas according to the equation $2C(\text{gas}) + N_2 = (CN)_2(\text{gas})$ is found to be $\Delta F_{298} = 87{,}580$.　　　　　H. M. D.

The Oxidising Power of Cyanates and the Free Energy of Formation of Cyanides. GILBERT N. LEWIS and THOMAS B. BRIGHTON (*J. Amer. Chem. Soc.*, 1918, **40**, 482—489).—The experiments described were undertaken with the object of providing data for the calculation of the free energy of formation of hydrogen

cyanide, a substance which is of considerable importance in connexion with the determination of the free energy changes associated with many different types of organic reactions.

Fused potassium cyanide is oxidised by carbon dioxide, and the fused cyanate is reduced by carbon monoxide. The equilibrium condition resulting from these opposed reactions has been examined by determining the value of $K = [CO_2]/[CO]$ for the gas mixture in equilibrium with the eutectic mixture of potassium cyanide and potassium cyanate at various temperatures between 721° and 847° (abs.). Preliminary experiments showed that the eutectic temperature is 555° (abs.), and that the mixture contains 14·6% of potassium cyanide. When the values of K are plotted against $1/T$, a straight line is obtained, and by extrapolation to the temperature of the eutectic point this gives $K = 0·89$. From this value of K, the free energy of the reaction KCNO(solid) + CO(gas) = KCN(solid) + CO_2(gas) is found to be $\Delta F_{555} = 126$. This, in combination with the value for the heat of the reaction at the ordinary temperature $\Delta H = 4300$ cal., gives $\Delta F_{298} = 2060$ for the free energy of the reaction at 25°.

From solubility and freezing-point data, the free energy change associated with the conversion of the solid salts into the corresponding ions in normal concentration has been found to be $\Delta F_{298} = -2130$ for potassium cyanide and $\Delta F_{298} = -1440$ for potassium cyanate. By combination of these results with the previous one, the free energy of the change CNO′ + CO(gas) = CN′ + CO_2(gas) is found to be $\Delta F_{298} = 1370$.

From this and free energy values previously derived, it follows that for the reaction C(gas) + $\frac{1}{2}N_2$ + ⊙ = CN′, $\Delta F_{298} = 35,277$, and since the free energy of formation of the hydrogen ion is taken as zero, we have for $\frac{1}{2}H_2$ + C(gas) + $\frac{1}{2}N_2$ = H˙ + CN′, $\Delta F_{298} = 35,277$. This result, in combination with $\Delta F_{298} = 11,856$ for the free energy of the reaction HCN(aq.) = H˙ + CN′, gives for the free energy of formation of hydrogen cyanide in accordance with the equation $\frac{1}{2}H_2$ + C(gas) + $\frac{1}{2}N_2$ = HCN(aq.) the value $\Delta F_{298} = 23,421$.

H. M. D.

Gas Dilatometer for ascertaining Decomposition Points.

W. C. MOORE and J. B. DAVIES (*Met. and Chem. Eng.*, 1918, **18**, 301—304).—The substance examined is heated in a vacuous glass test-tube placed vertically in a paraffin bath. Distillation products pass into a horizontal pipette-shaped air condenser sealed on to the test-tube and closed at the other end by a U-shaped manometer filled with mercury. The pressure in the apparatus is plotted as the temperature rises. A discontinuity in the curve due to the rapid evolution of permanent gas is taken as the decomposition point. The results are influenced by rate of heating, but when this was 1° per minute up to 150° and then slower, the following results were obtained : sucrose 178°, dextrose 177°, and soluble starch 214°, whilst with cellulose (filter paper) a slow decomposition commenced at 143°, with further points at 185° and 204°.

H. J. H.

Compressibility and Dilatability of Gases. A. LEDUC (*Ann. Physique*, 1918, [ix], **9**, 5—28).—A detailed description of a piezometer which can be used to observe the gases successively at pressures of 1, 2·8, and 5 atmos., which has been used for neon and argon. The following are the values of the constants found for neon: coefficient of departure from Mariotte's law, $-6 \cdot 10^{-6}$ per cm. of mercury at 17° between 1 and 5 atmos.; molecular volume at 0° and 760 mm., 1·0004; atomic weight, 20·15; coefficient of dilatation, $\beta = 3664 \cdot 10^{-6}$ between 5° and 30°. For argon the values are: coefficient of departure from Mariotte's law, $10 \cdot 2 \cdot 10^{-6}$ between 1 and 5 atmos.; molecular volume, 0·9990 at 0° and 760 mm.; atomic weight, 39·91 ± 0·01; coefficient of dilatation, $\beta = 3669 \cdot 10^{-6}$ between 8° and 32°. W. G.

Fluidity and Specific Volume of Aqueous Solutions. W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **102**, 173—176. Compare A., 1917, ii, 361).—Curves are given showing that, for aqueous solutions of a number of acids, for example, sulphuric and acetic, alkalis such as sodium and potassium hydroxides, hydrolysed salts such as sodium carbonate and ferric chloride, and neutral substances such as sucrose, there is a direct proportionality between the fluidity expressed in *C.G.S.* units and the specific volume. Even in the case of mixed solutions, for example, a solution containing sodium and copper sulphates, the proportionality holds.
E. H. R.

Soap Solutions. III. VICTOR LENHER and GEORGE H. BISHOP (*J. Physical Chem.*, 1918, **22**, 95—98).—The adsorption of sodium oleate by Ceylon graphite, willow charcoal, and animal charcoal has been examined by filtering a $N/10$-solution through 30 cm. columns of the principal materials. Successive fractions of the filtered liquid were analysed, and the process continued until no further adsorption occurred. The results show that animal charcoal has a much greater adsorbent capacity than wood charcoal, which, in turn, adsorbs sodium oleate more readily than graphite.
H. M. D.

Theory of Dyeing. H. R. KRUYT and (MISS) J. E. H. VAN DER MADE (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 636—641). —The observations recorded by Reinders (A., 1913, ii, 836) have led the authors to investigate further the influence of various salts on the distribution of dyes between water and *iso*butyl alcohol.

Experiments made with crystal-violet, magenta and methylene-blue, and the sodium salts of different acids show that the sequence of the anions, when arranged according to their influence on the distribution of the basic dye, is identical with the lyotropic series. This sequence is no longer found when acid dyes are substituted for the basic dyes.

The influence of salts on the adsorption of dyes by blood charcoal has also been examined. In the case of methylene-blue-B

extra and auramine-O, the order is not that of the lyotropic series, and it is supposed that the electrical charges of the ions have a preponderating influence. With crystal-violet, on the other hand, the sequence of the sodium salts is that of the lyotropic series. [See, further, *Ind.*, 238A.]   H. M. D.

A New Method for the Measurement of the Coefficient of Diffusion of Electrolytes.
St. PROCOPIU (*Ann. Physique*, 1918, [ix], **9**, 96—112).—In a broad, vertical tube are superposed two layers of different concentration of the same electrolyte, and the variation of a physical or chemical property, at a given distance from the surface of contact with the time is estimated. In this case, the *E.M.F.* between an electrode of the metal contained in the electrolyte and a similar electrode at a much greater distance is studied, and the time taken for it to reach its maximum is determined. Then $D = x^2/2\theta$, where D is the coefficient of diffusion, x is the distance of the first electrode from the surface of contact, and θ is the time taken for the *E.M.F.*, and consequently the concentration at x, to attain its maximum.   W. G.

Experiments on the Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials.
S. L. BIGELOW and C. S. ROBINSON (*J. Physical Chem.*, 1918, **22**, 99—127).—The experiments described were made with the object of ascertaining whether osmotic effects are exhibited under conditions which seem to preclude the possibility of chemical reaction between the membrane and the solvent. For this purpose, membranes were constructed from silica, graphite, amorphous carbon, copper, silver, and gold in a very finely divided state. These materials were compressed into the form of disks, which served to separate the solvent and solution. A special type of osmotic cell was devised which appeared to be adapted to the use of membranes of this type.

Preliminary results obtained for sucrose solutions (0·5 to 2 molar) are recorded which show that small osmotic effects are exhibited with these chemically inert membranes. By varying the degree of compression of the disks, the diameter of the pores could be altered, and it has been found that such variations are accompanied by a change in the osmotic effect in the sense that this increases with diminution in the size of the pores.

With copper membranes, negative osmotic effects have been observed. Similar results have been previously recorded for kaolin membranes.   H. M. D.

Crystal Structure of the Alums and the Rôle of the Water of Crystallisation.
L. VEGARD and H. SCHJELDERUP (*Ann. Physik*, 1917, [ii], **54**, 146—164).—Bragg's method has been applied in the investigation of the crystal structure of the alums by observations on crystals of potassium alum, ammonium alum, iron ammonium alum, and chrome alum. Using the rhodium line

$\lambda = 0.607 \times 16^{-8}$ cm., the authors measured the relative intensities of the spectra of different orders obtained by reflection from the (100), (110), and (111) planes, and from the results have deduced the probable arrangement of the metal, sulphur, and oxygen atoms in the space-lattice system. For a description of the rather complicated structure, the original paper must be consulted.

The crystal model divides the twenty-four molecules of water into six groups, which groups are cubically disposed with reference to the four tetrahedrally arranged atoms of sulphur. The model makes no distinction between the water of crystallisation and the other constituents of the alum. Any hypothesis which would distinguish the water of crystallisation from water of constitution could not be reconciled with the observed relations between the high-frequency reflection spectra. The removal of the water of crystallisation is necessarily accompanied by the destruction of that structure which is characteristic of the hydrated salt.

The zeolites obviously present an attractive material for investigation in regard to the influence of the water content on the crystalline structure, and observations of a preliminary character have been made on chabasite, crystals of which were dehydrated by heating at 200—300°, and examined before and after dehydration by the X-ray method. The results show that the relative intensities of the spectra of different orders are not appreciably altered by the loss of water. The dehydration is, however, accompanied by a diminution in the absolute intensities, and more particularly by a decrease in the sharpness of the maxima.

The assumption that the water molecules do not form an essential part of the space lattice of the zeolite is held to be inadmissible. The facts can be accounted for by the hypothesis that the weakened reflection of the partly dehydrated crystals is due to crystal elements which have not lost water, and retain therefore their original configuration. Crystal elements which have lost water and from which new structures have been formed are presumably orientated in all possible directions, and for this reason play a minor part in the effective reflection of the X-rays.

H. M. D.

In-, Uni- and Bi-variant Equilibria. XVIII. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 659—667. Compare A., 1917, ii, 454).—A further discussion of the equilibrium relations in systems of n-components with n-phases at constant temperature with varying pressure. The properties of such systems are very similar to those which have already been described for conditions in which the pressure is constant and the temperature variable. H. M. D.

One-sided Chemical Equilibria. E. BAUR (*Schweiz. Chem. Zeit.*, 1918, ii, 25—26).—When salicylic acid is heated at 200°, it volatilises, and the vapour undergoes partial dissociation into phenol and carbon dioxide. The degree of dissociation is dependent

on the pressure and follows the law of mass action, $P \cdot a^2/1 - a^2 = K = 254 \cdot 9$, where P is the pressure in cm. of mercury and a is the measured degree of dissociation. Although the dissociation is correctly described as an equilibrium, yet no synthesis of salicylic acid from phenol and carbon dioxide can take place in the gaseous condition. Hence the reaction, being irreversible, is a "one-sided" equilibrium. Another instance of a similar phenomenon has been observed in the formation and decomposition of phloroglucinol-carboxylic acid. Phloroglucinol and potassium hydrogen carbonate in aqueous solution give a partial formation of potassium phloro-glucinolcarboxylate. At 50°, the equilibrium is adjustable from both sides and follows the law of mass action. When the velocity of the changes, on the one hand the formation and on the other the decomposition, of the carboxylate is studied in solutions satu-rated with phloroglucinol, it is found that for the expression $V = K(C - C_1)$, where C is the momentary and C_1 the equilibrium concentration of the carboxylate, the value of K is about one-fourth in the formation of its value in the decomposition. This is explained on the ground that the decomposition of the carb-oxylate may take place in two ways, directly and by way of an intermediate ester salt, potassium phloroglucinol carbonate, whereas the formation of the carboxylate can only take place in one way, namely, through this intermediate stage. If this way through the ester salt did not exist, the carboxylate could decompose, but not re-form, yet the limit of the decomposition must be the same as it actually is where both ways are available.   J. F. B.

Reversible Reactions of Sulphur Compounds. GILBERT N. LEWIS, MERLE RANDALL, and F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 356—362).—An account is given of preliminary experiments which were undertaken with the object of finding reversible reactions suitable for the investigation of the free energy changes of sulphur compounds.

Towards aqueous solutions of various salts, sulphur begins to exhibit considerable reactivity when the mixtures are heated at 150° to 200°. Mercuric, ferric, and stannic salts are quantitatively reduced, and mercurous, cupric, bismuth, and lead salts are slowly but quantitatively precipitated as sulphides. Nitrate, per-manganate, iodate, and bromate ions are reduced to nitric oxide, manganese dioxide, iodine, and bromine respectively. Chlorates appear to be reduced very slowly, but sulphates, periodates, and perchlorates are not acted on at 180°. The reactions in question are probably due to the reversible change $2H_2O + 3S = 2H_2S + SO_2$, the sulphur dioxide being the active reducing agent.

Solid sulphates are reduced by hydrogen at moderate tempera-tures, and the sulphate ion is reducible at about 150° by mild reducing agents.

The investigation of the decomposition of silver sulphite on heat-ing shows that the reaction does not occur in accordance with the equation $Ag_2SO_3 = Ag_2O + SO_2$, but that the solid product of the reaction is either a basic salt or a solid solution. In presence of

water, reaction takes place more rapidly in accordance with the equation $2Ag_2SO_3 = 2Ag + Ag_2SO_4 + SO_2$, this reaction being catalysed by the water. Sulphuric acid is then produced in consequence of the further reaction represented by $Ag_2SO_4 + SO_2 + 2H_2O = 2Ag + 2H_2SO_4$.

The potential of the sulphur dioxide electrode has also been examined by measuring the *E.M.F.* of the cell $Pt | SO_2 | H_2SO_4 | Hg_2SO_4 | Hg$ for varying concentrations of the sulphuric acid and varying partial pressures of the sulphur dioxide. It has not been possible to find a satisfactory interpretation of the results obtained.

<div align="right">H. M. D.</div>

Equilibrium in the Reaction between Water and Sulphur at the Boiling Point of Sulphur. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1918, **40**, 362—367).—The equilibrium in the system $2H_2O + 3S = 2H_2S + SO_2$ has been examined at the boiling point of sulphur. The experiments were made in the presence of an excess of sulphur, and in these circumstances the partial pressure of this compound was constant. A weighed quantity of water, enclosed in a thin-walled sealed tube, was introduced into the reaction chamber, consisting of a glass bulb of known capacity, which was heated in the vapour of boiling sulphur. The formation of hydrogen sulphide and sulphur dioxide is accompanied by an increase in the pressure when the volume of the reaction mixture is kept constant, and the pressures required to maintain this condition were measured in a series of experiments in which varying quantities of water were introduced into the reaction bulb. From these pressures, it is possible to calculate the partial pressures of the hydrogen sulphide, sulphur dioxide, and water in the reacting mixture.

Some difficulties were met with by reason of the fact that the water adsorbed by the surface of the glass is partly given off at the temperature of the experiments, but suitable allowance was made for the effect thereby produced.

The results obtained in six experiments gave values of $K = [H_2S]^2[SO_2]/[H_2O]^2$ varying from 0.00088 to 0.00232. The differences between these results are not considered excessive when the multiplication of errors, which the formula involves, is taken into account. The mean value $K = 0.00154$ may be used in the calculation of the free energy of formation of sulphur dioxide.

<div align="right">H. M. D.</div>

Equilibrium in the Reaction between Water and Sulphur at High Temperatures. The Dissociation of Hydrogen Sulphide. MERLE RANDALL and F. RUSSELL VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 368—375. Compare preceding abstract).—The equilibrium in question has been further investigated at higher temperatures, where free hydrogen is formed by the dissociation of the hydrogen sulphide. The equilibrium mixture contains, therefore, the five gases, water, sulphur, hydrogen

sulphide, sulphur dioxide, and hydrogen. If the dissociation constant of hydrogen sulphide is known, the composition of the equilibrium mixture of the five gases can be calculated if the original composition of the mixture, the total pressure, and the partial pressure of one of the five gases are determined.

The partial pressure of the hydrogen has been measured by the use of an evacuated platinum bulb inserted into the reaction chamber, into which the hydrogen diffused until the pressure in the bulb became equal to the partial pressure of the hydrogen in the gas mixture. This apparatus was used in the extension of previous measurements of the dissociation of hydrogen sulphide to higher temperatures. The values obtained for $K_p = [H_2S]/[H_2][S_2]^{\frac{1}{2}}$ when the pressures are measured in atmospheres decrease from 7·98 at 1362° (abs.) to 1·81 at 1667° (abs.). These results agree with the observations of Preuner and Schupp (A., 1909, ii, 977), whose measurements extended to 1405° (abs.).

In the investigation of the more complex equilibrium, a mixture of gases of known composition was obtained by electrolysing a 10% solution of potassium hydroxide in two separate vessels, the oxygen from one or both of which could be passed over boiling sulphur and converted into sulphur dioxide. The currents passing through the electrolysers, which were placed in parallel, were accurately measured and afforded the data for the calculation of the composition of the original mixture. Since the experiments were made at atmospheric pressure, the further quantity required was readily obtained.

The results obtained in experiments at temperatures ranging from 1160° (abs.) to 1645° (abs.) are used in the calculation of the logarithm of the equilibrium constant $K_p = [H_2O]^2[H_2S]/[H_2]^3[SO_2]$, corresponding with the equation $3H_2 + SO_2 = 2H_2O + H_2S$. The value of $\log K_1$ (partial pressures being measured in atmospheres) decreases from 5·93 at 1160° to 2·56 at 1645° (abs.).

H. M. D.

Studies in Esterification. X. The Esterification of Benzoic and the Toluic Acids by Methyl, Ethyl, and Propyl Alcohols. RAYMOND FREAS and E. EMMET REID (*J. Amer. Chem. Soc.*, 1918, **40**, 569—578).—A re-examination of the position of equilibrium attained by various mixtures of methyl, ethyl, or propyl alcohol with benzoic or one of the toluic acids, or by mixtures of the esters with water. The binary mixture, of known composition, was in each case sealed in a glass tube and heated for four or eight days at 200°, the proportion of acid in the final mixture being then estimated and the percentage of equivalent amounts esterified or hydrolysed at equilibrium calculated by the formula given by Faber and Reid (A., 1917, i, 626). Under these conditions, it is found that with mixtures of any pair of the above alcohols and acids, or of one of the esters with water, in varying proportions, the position of equilibrium accords closely, although not exactly, with the law of mass action, this result agreeing with that of Berthelot and Pean de St. Gilles. Of the toluic acids, the

ortho-compound shows the least and the para-compound the highest esterification limit towards methyl alcohol, but the reverse is true of the esterification limits towards ethyl and propyl alcohols; the esterification limit of any one of the four acids is lower towards ethyl alcohol than towards propyl or methyl alcohol, the latter giving the highest value with each of the acids.　　D. F. T.

The Hydrolysis of Methyl Sulphate and Ethyl Sulphate with Sodium Methoxide or Ethoxide. J. POLLAK and A. BAAR (*Monatsh.*, 1918, **38**, 501—523).—Methyl sulphate undergoes hydrolysis by water more rapidly than ethyl sulphate (Claesson, A., 1879, 775; Kremann, A., 1907, ii, 241), but in the presence of potassium hydroxide the ratio of the reaction velocities is very different from that observed for the hydrolysis by water only. With $0.5N$-potassium hydroxide at 25°, the unimolecular constant for methyl sulphate is forty-five times as great as for the ethyl ester, whereas with water only the ratio is approximately $5:1$. In order to decide whether the difference is due to the difference in the solubility of the two esters in water, and to avoid the possibility of such a disturbing factor, it is desirable to examine the rate of reaction in a homogeneous system. Kremann (A., 1907, ii, 157) has already observed that with methyl and ethyl alcohol, the rate of reaction of methyl sulphate is three to four times that of ethyl sulphate. With an alcoholic solution of sodium ethoxide, however, at 25° methyl sulphate reacts approximately twenty-five times as rapidly as ethyl sulphate, whilst at 0° the ratio is $58:1$. The reaction in each case proceeds as far as the corresponding alkyl hydrogen sulphate or its sodium salt, any further hydrolysis being negligble. These results demonstrate that the great difference in the velocities of reaction of alkali on the two alkyl sulphates is not mainly due to any difference of solubility on the part of the sulphates, because a similar difference is observed in homogeneous and in heterogeneous systems. The difference is therefore presumably to be attributed to the different character of the reactions, the alkali hydrolysis yielding the alkali salt of the alkyl hydrogen sulphate, whilst the free alkyl hydrogen sulphate is produced by the action of water or of alcohol.

Examination of the reaction velocity of ethyl and methyl sulphates with alcohol in the presence of a gradually increasing proportion of water shows that the former ester is distinctly less soluble in water, and that the difference in the solubility of the two esters may exert an appreciable influence on the relative apparent reactivity of the two esters towards alkali hydroxide in the heterogeneous aqueous system. Methyl alcohol reacts with the two alkyl sulphates more rapidly than does ethyl alcohol, and although it was found that, as expected, sodium methoxide affects the methyl ester much more rapidly than the ethyl ester, the surprising result was obtained that sodium methoxide in methyl-alcoholic solution is less reactive than an ethyl-alcoholic solution of sodium ethoxide. A similar observation to this has already

been made in certain cases, for example, by Lobry de Bruyn and Steger (A., 1899, i, 745, 849), Steger (A., 1889, i, 745), and Kremann (A., 1905, ii, 307), but the suggestion of the last-named, that the difference is due to the presence of traces of water which cause a greater proportion of hydrolysis in the sodium ethoxide, is discredited, and the suggestion is made that the explanation may be found in the possible occurrence of the reaction between the alkyl sulphate and the undissociated portion of the sodium alkoxide (compare Wegscheider and Amann, A., 1915, ii, 757).   D. F. T.

The Velocity of Formation of Nitrosyl Bromide, $2NO + Br_2 = 2NOBr$. MAX TRAUTZ and VASANJI P. DALAL (*Zeitsch. anorg. Chem.*, 1918, **102**, 149—172. Compare A., 1916, ii, 304, and this vol., ii, 151).—The investigation of this reaction was limited to temperatures between $-15°$ and $+15°$, to bromine pressures of 11—26 mm., and nitric oxide pressures of 11—12 mm.   At greater temperatures or pressures, nitrosyl bromide decomposes, and at lower temperatures the bromine condenses on the glass of the vessel.   In presence of excess of bromine, the reaction appears to be of the third order, the velocity constants found lying between $0·9$ and $1·6 . 10^{10}$.   Probably, however, there are two superimposed reactions, the first, $NO + Br_2 \rightleftharpoons NOBr_2$, coming to equilibrium very quickly, whilst the second, $NOBr_2 + NO \rightleftharpoons 2NOBr$, is measurable.   The temperature coefficient is very small, apparently slightly greater than unity, and could not be determined with certainty.   On the supposition that the reaction takes place in the above two stages, the "heat of activation" is calculated, and is found to be 3076 cal.   The velocity constants calculated from this number agree substantially with the observed values and support the authors' theory of thermochemical processes.   E. H. R.

Velocity of Dissolution of the Metals in Acids.   III. Velocity of Dissolution of Alloys of Zinc with Arsenic, Lead, Cadmium, Nickel, Platinum, and Gold. M. CENTNER-SZWER (*Zeitsch. physikal. Chem.*, 1918, **92**, 563—580. Compare A., 1914, ii, 550; 1915, ii, 158).—The observations previously made on the rate at which hydrogen is evolved from solutions of hydrochloric acid by zinc–copper alloys have been extended to alloys of zinc with other metals.   The results obtained show that arsenic, lead, and cadmium produce no increase in the rate of dissolution of the zinc.   The contrary observations recorded by previous observers are attributed to the presence of traces of other metals— probably iron or copper.   The facts established by the author's experiments are difficult to reconcile with the theory of local elements.

Very small quantities of nickel, platinum, and gold of the order of 0·01% produce an appreciable increase in the rate of dissolution of zinc.

The results obtained lead to the conclusion that pure zinc is

not acted on by either hydrochloric or sulphuric acid if the concentration is less than about 0·5 to 1N. H. M. D.

Method for the Carrying Out of Catalytic Reactions.
JOHANN WALTER (D.R.-P., 295507; from *Chem. Zentr.*, 1917, i, 291).—Thorough exposure of the catalyst to the reagents is achieved by electromagnetic means. The catalyst itself may be magnetic and if desired spread on a non-magnetic material, or a non-magnetic catalyst may be deposited on a magnetic substance, and parts of the apparatus, such as baffle plates or gauze in a gas tube, or mechanical agitators, are made magnetic or magnetisable. During the reaction, or during the removal of the products, magnetic fields are established and broken by electrical means, so that the catalyst is kept moving, but near the exit of the apparatus a permanent field is maintained to prevent loss of the agent as dust. Examples given in the original specification include the hydrogenation of train oil, the preparation of methane from carbon monoxide, and the reduction of cinnamaldehyde to β-phenylpropaldehyde and β-phenylpropyl alcohol, lævulose to mannitol, and quinine to di- and tetra-hydroquinine. J. C. W.

Some Problems of Atomic Stability.
J. W. NICHOLSON (*Proc. Physical Soc. London*, 1918, **30**, 65—82).—The author has investigated the dynamical stability of model atoms of pyramidal form consisting, for example, of a nucleus, a ring of electrons in the form of a circle the axis of which passes through the nucleus, and a single stationary electron on this axis. It is shown that no positively charged or neutral atom can exist in this form. Such structures are incompatible with a steady rotation of the ring electrons and cannot well form part of any molecular structure. The results appear to vitiate completely the molecular structures which have been formulated by Stark. H. M. D.

Molecular Frequency and Molecular Number.
H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 338—349).—In a previous paper (compare this vol., ii, 14) it has been shown that the atomic number of an element is related to its characteristic frequency. Similar considerations have been applied to compounds, and it is shown that the formulæ $Nv = nv_A$ and $Nv = (n + \frac{1}{2})v_A$ represent the relations between the molecular number N and the characteristic frequency v calculated from the specific heat at low temperatures or from Lindemann's formula. In these formulæ, n is an integer and v_A the fundamental atomic frequency $= 21 \times 10^{12} (\text{sec.}^{-1})$.

The molecular number N of a compound $A_aB_bC_c$ is given by the equation $N = aN_a + bN_b + cN_c$, in which N_a, N_b, and N_c are the atomic numbers of the component elements. Evidence in support of the above formulæ connecting N and v has been obtained by reference to the data for both inorganic and organic compounds. The agreement is such that the relations cannot be regarded as fortuitous.

It is suggested that the integer n (the frequency number) is related to the number of valency electrons which are concerned in imparting to the solid its crystalline structure.   H. M. D.

Glauber's Period in Amsterdam. W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 268—271).—The register of the Western Church at Amsterdam records that "Johan Rudolph Glaubar" was interred on March 10th, 1670, proving the inaccuracy of the statement made by Goossen van Vreeswyck ("Silvere Rivier," The Hague, 1684, p. 117) that his death occurred on March 19th, 1670.   A. J. W.

Berend Coenders Van Helpen; a Groningen Alchemist of the Seventeenth Century. F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 285—302).—An account of the life, work, and family of the alchemist Berend Coenders van Helpen, a typical landed proprietor of the seventeenth century, who was born at Groningen in June, 1601, and died at Copenhagen on January 3rd, 1678.   A. J. W.

Willem Homberg. F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 316—337).—An account of the life and a list of the publications of Willem Homberg, who was born in Batavia on January 8th, 1652, and died in Paris on September 24th, 1715.   A. J. W.

Arrangement for Illuminating a Chemical Balance. B. D. PORRITT (*J. Soc. Chem. Ind.*, 1918, **37**, 85T).—A "tubolite" metallic filament lamp of 16 candle-power and 8·5 inches long is fitted on the top of the balance case; the lamp is enclosed in a semi-circular aluminium reflector, which serves to direct the light through the glass top of the case on to the beam and to screen the lamp from the eyes of the person using the balance.   W. P. S.

Inorganic Chemistry.

Production of Oxygen Free or almost Free from Chlorine. CHEMISCHE FABRIK GRÜNAU, LANDSHOFF & MEYER, EMIL FRANKE and FRIEDRICH SCHMIEDT (D.R.-P., 299505, 1915; from *Chem. Zentr.*, 1917, ii, 508).—By the addition of a small quantity of nickel or cobalt in the form of metal, oxide, or salt, the "first period" of development of oxygen from chlorates or perchlorates is prolonged; cerium dioxide also can be used as catalyst. The last traces of chlorine can be removed from the gas by passing this through a filter of magnesium oxide, whiting, or anhydrous sodium carbonate, which may be distributed over some inert material, such as glass wool or asbestos. 　　　　D. F. T.

A Hydrogen Sulphide Generator. L. SATTLER (*J. Ind. and Eng. Chem.*, 1918, **10**, 226).—The main generator consists of a large aspirator bottle the bottom tubulure of which is fitted with a straight stop-cock connected with one of the tubulures of a three-neck Woulfe bottle. Through the central orifice of the latter a tube passes to the bottom of the bottle and is connected by a rubber tube to an aspirator bottle placed at a higher level, which governs the pressure under which the apparatus works. The third orifice of the Woulfe bottle serves for the passage of a siphon tube with stop-cock through which the waste acid can be discharged. The upper tubulure of the main generator carries a T-piece, one branch of which is connected with a tube dipping under mercury forming a safety-valve seal against excessive pressure. The other branch of the T-piece leads the generated gas through a stop-cock to a lead pipe terminating in a perforated coil submerged in a washing bottle, through which the washed gas is delivered for use. The main generator is charged with about 23 kilos. of iron sulphide and the high-level acid reservoir with about 14 litres of hydrochloric acid diluted 1:1 by volume. On opening the stop-cocks leading to and from the main generator, the three-neck mixing bottle should be filled with acid, and about 7·5 cm. of the acid should remain in the reservoir. J. F. B.

Synthesis of Ammonia at High Temperatures. EDWARD BRADFORD MAXTED (T., 1918, **113**, 168—172).—From a rough calculation of the equilibrium between nitrogen, hydrogen, and ammonia, made by extending Haber's formulæ to temperatures above 1000° abs., it appears that increase of temperature leads at first to a rapid decrease in the proportion of ammonia until a minimum is reached, after which further increases cause the yield of ammonia to rise with increasing velocity. It should be possible, therefore, to realise a fair production of ammonia by heating mixtures of hydrogen and nitrogen to high temperatures and suddenly cooling the hot gases.

The subject has been examined experimentally by igniting mixtures of nitrogen, hydrogen, and oxygen in a tube (*a*) under water, so that the hot gases were cooled by the water itself, or (*b*) cooled externally by being made the tube of a Liebig's condenser. The direct cooling (*a*) proved to be far more efficient, and with a mixture of gases in the proportions $N : H : O = 1 : 43 : 20$, giving a flame with temperature 2580° abs., the yield of ammonia was as much as 1·23% at atmospheric pressures.

For experimental details, see the original. J. C. W.

Preparation of Carbon Monoxide. BERTRAM BLOUNT (*Analyst*, 1918, **43**, 88).—Fairly pure carbon monoxide, free from carbon dioxide, may be obtained by heating a mixture of calcium oxalate and calcium oxide. The gas usually contains some sulphur dioxide if it is prepared from potassium ferrocyanide and sulphuric acid, or carbon dioxide if made from oxalic acid and sulphuric acid. W. P. S.

Preparation of Argon in the Laboratory. MAX BODENSTEIN and LILI WACHENHEIM (*Ber.*, 1918, **51**, 265—270).—Samples of oxygen prepared from the air usually contain argon, occasionally as much as 3%. The commercial product can therefore be used as a source of argon, the oxygen being removed by combination with hydrogen. For this purpose, the authors have designed an apparatus, which is described and figured in the text. The control of the process requires a certain amount of manipulative skill, but even on the laboratory scale it only takes about two hours to prepare a litre of argon.

The hydrogen and oxygen, supplied from cylinders with good valves, are led into a small quartz combustion chamber through gas current manometers, the water is then trapped in two condensers, and the issuing gas made to pass through a sensitive gas current manometer. If this records minimum rate of flow, it indicates that neither oxygen nor hydrogen is being supplied in excess; if not, the gases are regulated accordingly. After this manometer are placed a hot tube containing copper oxide and copper to trap any traces of uncombined gases, then another condenser for the water, and finally an iron gas-washing tube containing calcium turnings heated electrically to 600°. This serves to absorb any nitrogen that may be present.

The process is based on a method described by the Griesheim-Elektron Co., D.R.-P., 295572 of 1913.   J. C. W.

Production of Mono-, Di- and Tri-metallic Alkali Perphosphates and Perarsenates. S. ASCHKENASI (D.R.-P., 299300, 1914; from *Chem. Zentr.*, 1917, ii, 438).—By the addition of the necessary quantity of alkali to a solution of barium peroxide in aqueous arsenic or phosphoric acid, barium arsenate or phosphate is precipitated, and the filtrate containing the per-salt is then evaporated with slight warming and under reduced pressure; an aqueous solution of a mixture of sodium peroxide with the primary or secondary alkali salts can also be submitted to evaporation. If a solution of an arsenate, phosphate, or borate in dilute hydrogen peroxide is evaporated to dryness with gentle warming and under reduced pressure, the corresponding per-salt, for example, sodium perborate, can be obtained with scarcely any loss of oxygen.

D. F. T.

Influence of Calcium Sulphate on the Corrosive Action of Water on Iron. P. MEDINGER (*Ber.*, 1918, **51**, 270—271).—The fact that gas and water mains suffer corrosion particularly severely in heavy clays which contain calcium sulphate is explained as follows: through the ionisation of the sulphate, the proportion of calcium ions in solution becomes so great that the dissociation of the calcium hydrogen carbonate is depressed, and, consequently, the production of H and HCO_3 ions from the free carbonic acid is not so much hindered. The enhanced acidity of a solution containing free carbonic acid and calcium hydrogen carbonate con-

sequent on the addition of calcium sulphate may be demonstrated by means of litmus.   J. C. W.

Iron Trisulphide. WERNER MECKLENBURG and V. RODT (*Zeitsch. anorg. Chem.*, 1918, **102**, 130—148).—The work of previous investigators has left undecided the question of the existence of ferric sulphide. The authors have studied the action of hydrogen sulphide on ferric hydroxide, of alkali sulphides on ferric salts, and of alkali polysulphides on ferrous salts. When hydrogen sulphide is passed for a long time (about twelve hours) through an aqueous suspension of freshly prepared ferric hydroxide at the ordinary temperature in absence of air, the colour of the hydroxide gradually becomes black, and when the reaction is 'finished, the composition of the precipitate corresponds with Fe_2S_3, aq. The precipitate contains no sulphur soluble in carbon disulphide and is completely decomposed by dilute hydrochloric acid, forming ferrous chloride, hydrogen sulphide, and sulphur. Treatment with carbon disulphide, however, changes the character of the trisulphide, rendering it partly insoluble in dilute hydrochloric acid. The hydrated trisulphide is rapidly decomposed by air, and in absence of air it undergoes spontaneous decomposition into ferrous sulphide and iron disulphide. It can be completely dried in a vacuum over phosphoric oxide. The anhydrous trisulphide is pyrophoric if suddenly brought into contact with air, but if spontaneous ignition is prevented, it is quite stable.

By addition of a solution of a ferric salt to excess of sodium sulphide solution, a precipitate is produced having the composition Fe_2S_3,Na_2S, and the same compound is formed by the action of excess of sodium polysulphide solution on a solution of a ferrous salt. The alkali sulphoferrites form dilute aqueous colloidal solutions having a deep green colour.   E. H. R.

Reactions in Non-aqueous Solvents. II. The Action of Chromyl Chloride on Phosphorus Haloids. HARRY SHIPLEY FRY and JOSEPH L. DONNELLY (*J. Amer. Chem. Soc.*, 1918, **40**, 478—482).—The action of chromyl chloride on phosphorus di-iodide, tri-iodide, pentachloride, and pentabromide in anhydrous carbon tetrachloride has been examined.

With phosphorus di-iodide, a brown-coloured additive compound, CrO_2Cl_2,PI_2, is precipitated. It is readily decomposed by water with liberation of iodine and the formation of a solution containing phosphate, chromic, chloride, and iodide ions.

Phosphorus tri-iodide also yields an additive compound, CrO_2Cl_2,PI_3, which, when dry, consists of a purplish-red powder. It is decomposed by water in accordance with the equation
$2CrO_2Cl_2,PI_3 + 4H_2O = 4HCl + 4HI + 2CrPO_4 + I_2$.

With phosphorus pentachloride, the additive compound CrO_2Cl_2,PCl_5 is produced in the form of a yellowish-red powder readily decomposed by water.

It has been previously found (A., 1916, ii, 626) that phosphorus

tribromide reacts according to the equation $2CrO_2Cl_2 + 3PBr_3 = 2CrOCl,POBr_3 + PBr_3Cl_2$, and the product obtained by interaction of chromyl chloride with phosphorus pentabromide appears to be a mixture of $CrOCl,POBr_3$ and the additive compound CrO_2Cl_2,PBr_5. The formation of these substances is presumably connected with the fact that phosphorus pentabromide is measurably dissociated into the tribromide in carbon tetrachloride solution.   H. M. D.

The Reaction between Antimony and Solutions of Sodium in Liquid Ammonia. EDWARD B. PECK (*J. Amer. Chem. Soc.*, 1918, **40**, 335—347).—Metallic antimony dissolves when brought into contact with a solution of sodium in liquid ammonia. The atomic ratio of antimony to sodium in the saturated solution increases from about 1·2 for a solution containing 0·005 gram atom of sodium per litre to about 2·3 for a solution containing 0·4 gram atom of sodium per litre. For more concentrated solutions, the ratio diminishes slightly. The diminution may be due to the failure to reach equilibrium in the more concentrated solutions which are highly viscous, or it may possibly be accounted for by the fact that the solution was assumed to have the same volume as the ammonia which it contained.

The observed facts suggest that there are at least two compounds formed, in one of which the ratio Sb : Na is greater than two, whilst in the other this ratio is less than two.

The electrolytic behaviour of these solutions, when subjected to the action of a current between a platinum anode and an antimony cathode, has also been examined, but the quantitative data do not permit of any definite conclusion. The results show, however, that antimony is present in the solutions as anion, and that more than one atom of antimony is associated with each negative charge.

                                                   H. M. D.

A New Metastable Form of Antimony Tri-iodide. A. C. VOURNASOS (*Compt. rend.*, 1918, **166**, 526—528).—Antimony tri-iodide, regarded as trimorphous, may be obtained in a fourth form by cooling a hot saturated solution of the red iodide in glycerol. It is thus obtained as an amorphous, yellow powder, m. p. 172°, at which temperature it steadily passes into the red variety, forming hexagonal crystals. This metastable, amorphous form may also be obtained from the red form by warming it on a water-bath with fifteen times its weight of acetic acid and a little potassium acetate. The solution on cooling deposits the yellow, amorphous iodide. It may also be prepared from antimony tri-oxide and potassium iodide by heating them at 100° with an excess of anhydrous acetic acid. The last method also applies to the preparation of arsenic, antimony, and bismuth tribromides, and arsenic and bismuth tri-iodides.   W. G.

Mineralogical Chemistry.

The Gyrohedral Character of Rock Salt. R. GROSZ (*Centr. Min.*, 1918, 1—19).—The crystal structure deduced by W. H. and W. L. Bragg for sodium chloride and other similar salts is stated not to be satisfactory. On the one hand it is a holohedral structure, whilst there is abundant evidence that the structure of sylvine is gyrohedral hemihedral, and that other salts of the same series are certainly not holohedral; on the other hand, no account is taken of the chemical bonds between individual atoms. By symmetrically displacing the centres of gravity of selected atoms in the Bragg structure, a number of new structures can be produced having gyrohedral or tetartohedral symmetry, and it is claimed that these cannot be distinguished by *X*-ray analysis from the holohedral form. If rock salt were tetartohedral, irregularities might be expected to appear in the Laue radiogram, but such irregularities the author has failed to discover.

It has been shown by Smits and Scheffer (A., 1917, ii, 78) that it is possible to couple symmetrically the atomic valencies in a cubic structure of atoms of two kinds. The coupling leads to the formation of cubic aggregates of different sizes according to the disposition of the planes of atoms, and these aggregates may be regarded as crystal molecules. The structure derived by the association of such aggregates affords an explanation of the cubic cleavage of rock salt, since at regular intervals there occur in the series of {100} planes pairs of planes between which no chemical bonds are active. A crystal cleaved along these planes of zero affinity would contain no excess of uncombined atoms of either kind, whereas in other crystal models the "ideal" crystal always contains an excess of atoms of one kind.

The hemihedral character of the crystals of rock salt may also be accounted for by making certain assumptions regarding the axis and direction of rotation of the valence electrons about the individual atoms. E. H. R.

Algodonite and Whitneyite. L. H. BORGSTRÖM (*Geol. För. Förh.*, 1916, **38**, 95—100; from *Jahrb. Min.*, 1918, Ref. 11—13). —Analyses of algodonite and whitneyite from the Mohawk mine, Michigan, gave Cu 84·1 and 87·2% respectively. Melting-point determinations in capillary tubes showed a wide interval, sintering beginning at 695°, but fusion was complete only at 100° higher. These minerals are therefore decomposed before fusion takes place. The cooling curves of the fused materials show in each case a pronounced break at 688°, that is, near the freezing point (685°) of the eutectic Cu_3As—Cu. Polished plates of the natural minerals and of the fused products were etched with nitric acid and examined under the microscope. Algodonite was seen to consist of almost homogeneous crystalline material with very little metallic

copper, whilst whitneyite contains 3—4% of metallic copper, and thus consists of a mixture of algodonite and copper. The fused products in each case consist of a mixture of light grey Cu_3As and copper. The electrical resistance in ohms for rods 1000 mm. long and 1 sq. mm. cross-section is for whitneyite 0·341 and 0·335, for algodonite 0·415, and for the fused materials 0·469 and 0·634 respectively. Although not indicated on the cooling diagrams of copper–arsenic fusions, the copper arsenide, Cu_6As (algodonite), therefore exists, but is only stable below the point of fusion. On the other hand, the arsenide Cu_9As (whitneyite) has no existence.

<div align="right">L. J. S.</div>

Spectral Investigation of the Composition of Goyazite. A. DE GRAMONT (*Bull. Soc. franç. Min.*, **40**, 26; from *Chem. Zentr.*, 1917, ii, 825).—According to spectral observations, calcium, strontium, and probably aluminium are characteristic constituents of goyazite.   H. M. D.

Meerschaum from Kraubat, Styria. H. LEITMAIER (*Sitzungsber. K. Akad. Wiss. Wien, Math.-Nat. Kl.*, Abt. I, 1915, **124**, 163—180; from *Jahrb. Min.*, 1918, Ref. 21—22).—The meerschaum occurs as bands 1 mm. to 20 dcm. thick in massive magnesite. It is white, yellow, or green, and either earthy (being then mixed with magnesite), or compact with large-conchoidal fracture. Analysis of the latter variety gives the formula $2MgO,3SiO_2,4H_2O$. About half of this water is lost over sulphuric acid at 20°, and is reabsorbed from a moist atmosphere to the extent of 37·56% H_2O after 144 hours. At 100° the loss is 9·72%, and at 450° it is 18·17%. Since $2H_2O$ is more closely held, the formula is written $2MgO,3SiO_2,2H_2O$, any extra water present depending on the vapour tension of the surrounding atmosphere. The meerschaum and magnesite have probably originated by the action of carbonated waters on serpentine. When fused, the meerschaum gives rise to an enstatite containing an excess of silica ($MgO : SiO_2 = 7 : 9$), which is probably held in solid solution.   L. J. S.

The Identity of Shattuckite and Plancheite. F. ZAMBONINI (*Compt. rend.*, 1918, **166**, 495—497).—The mineral shattuckite as described by Schaller (*J. Washington Acad. Sci.*, 1915, **5**, 7) and the mineral plancheite as described by Lacroix (A., 1908, ii, 508) possess the same optical and crystallographic properties, although differing slightly in their chemical analyses. As a result of the examination of a specimen of plancheite, the author has obtained analytical data in agreement with those for shattuckite and for the composition $2CuSiO_3,H_2O$, and he considers that these two minerals are identical and that the older name plancheite should be retained.   W. G.

Gedrite from the Tatra Mountains, Hungary. W. PAWLICA (*Bull. Acad. Sci. Cracow, Cl. Sc. Math. et Nat.*, Ser. A, 1915, 18—25; from *Jahrb. Min.*, 1918, Ref. 19—20).—Analysis I is of a

gedrite-gneiss from the Gewont peak, containing quartz (41·3 mol. %), plagioclase (a basic oligoclase, $Ab_{72}An_{28}$, 35·3), gedrite (13·0), biotite (5·1), ilmenite (1·3). The gedrite (anal. II, mean of three) forms black, orthorhombic prisms $\frac{1}{2}$—3 cm. long and 0·1 mm. thick with distinct pleochroism, bluish-green to pale green. The high percentage of fluorine and water is not accounted for by the ordinary formula, but in Penfield's amphibole formula it figures in the molecule, $(F,HO)_2Mg(Al,Fe''')SiO_5$, which is here present to the extent of 39·6%, with the metasilicate molecules, $MgSiO_3$ (26·6), $FeSiO_3$ (25·7), $CaSiO_3$ (7·2), and Na_2SiO_3 (0·9%).

	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.
I.	69·82	1·24	0·18	12·70	2·32	2·78	0·12	2·96	2·47
II.	41·59	0·97	0·16	12·81	5·90	14·81	trace	3·55	15·13

	K_2O.	Na_2O.	F.	H_2O <105°.	H_2O >105°.	Total less O for F.	Sp. gr.
I.	0·40	3·27	0·17	0·23	1·30	99·89	3·240
II.	0·12	0·43	2·34	0·86	1·68	99·42	2·701

L. J. S.

Iron Silicate Ores of the Diabase and Schalstein Zone between Sternberg (Moravia) and Bennisch (Austrian Silesia). FRANZ KRETSCHMER (*Jahrb. Min.*, 1918, 19—42).—A detailed account is given of the characters of these ores as seen in micro-sections, an account of their chemical characters having been sent for publication in *Arch. Lagerstättenforsch., Berlin.* The dense, chloritic minerals of which these ores are composed include thuringite and moravite (A., 1906, ii, 458), and two new species, viridite and mackensite, differing from the former in containing more iron (respectively ferrous and ferric), and correspondingly less alumina. *Viridite* contains only 4·49% Al_2O_3, and approximates to the end-member $4FeO,2SiO_2,3H_2O$. It is a compact, leek-green ore, D 2·89, H 3—3½, and under the microscope is seen to consist of minute needles and scales with pearly, micaceous cleavage. *Mackensite* contains 6·14% Al_2O_3 (in part due to the presence of admixed thuringite), and approximates to the end-member, $Fe_2O_3,SiO_2,2H_2O$, of the thuringite series. It is compact, iron-black to greenish-black, D 4·89, H 3—3½, and under the microscope shows colourless or brownish-green needles surrounding shreds of thuringite and grains of calcite and magnetite. Locally, the magnetite is present in greater relative amount, but ores of this character are not abundant. L. J. S.

Analytical Chemistry.

Increasing the Delicacy of Delivery of Burettes. EWART
H. MERRITT (*Analyst*, 1918, **43**, 138).—Both the inside and the
outside of the jet of the burette are coated with a thin film of

paraffin (m. p. about 55°); the number of drops per c.c. delivered by the burette may be thus increased from twenty to forty.

W. P. S.

A New Process of Quantitative Analysis. ALBERTO BETIM PAES LEME (*Compt. rend.*, 1918, **166**, 465—467).—The method is a spectrographic one, using a screen having a narrow, horizontal opening and travelling with a constant velocity in a vertical direction during the vaporisation of a known weight of the mineral containing the element to be estimated. The width of the opening and the velocity of the screen are equal. A given ray for the element is adopted once and for all, and the time during which it is visible is determined. An example is given, aluminium being the metal to be estimated.   W. G.

Detection of Small Quantities of Chlorine in Iodine. J. PINKHOF (*Pharm. Weekblad*, 1918, **55**, 236).—The presence of chlorine in iodine between $\frac{1}{8}$% and 2% can be detected by neutralisation with thiosulphate and precipitation with barium nitrate of the sulphate formed.   A. J. W.

Estimation of Chlorides in Blood. MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 59).—Ten c.c. of the serum are mixed with 10 c.c. of 20% trichloroacetic acid solution, the mixture is filtered, and 10 c.c. of the filtrate are diluted with 25 c.c. of water, then acidified with 5 c.c. of nitric acid, and the chloride is titrated by Volhard's method.   W. P. S.

[Estimation of Sulphur in Ores, etc.] F. G. HAWLEY (*Eng. and Min. J.*, 1918, **105**, 385—386).—A method is described for estimating sulphur gravimetrically in ores and furnace products by oxidation to sulphate and precipitation as barium sulphate, which avoids the difficulties usually experienced in oxidising mattes and calcines, or ores containing much copper or zinc sulphide. The oxidising mixture employed is a 20% solution of sodium chlorate to which is added a small quantity of a mixture of equal parts of bromine and glacial acetic acid, followed by an equal volume of nitric acid nearly saturated with potassium chlorate. [For details, see *Ind.*, May.]   W. F. F.

Some Limitations of the Kjeldahl Method. HARVEY C. BRILL and FRANCISCO AGCAOILI (*Philippine J. Sci.*, 1917, **12A**, 261—265).—The Kjeldahl method yields low results when applied to the estimation of nitrogen in pyridine, piperidine, quinoline, *iso*quinoline, hydroxyquinoline, pyrrole, and sometimes in nicotine; this is possibly due to the formation of sulphonic derivatives, which resist decomposition. In the case of pyridine, the Gunning-Arnold method gives trustworthy results if the heating is prolonged for a considerable period (four hours) after the solution has become clear. Low results are always obtained when sodium sulphate is used in place of potassium sulphate for raising the boiling point of the mixture. [See, further, *Ind.*, 225A.]   W. P. S.

Kjeldahl's Method for the Estimation of Nitrogen.
EDUARD SALM and SIEGFRIED PRAGER (*Chem. Zeit.*, 1918, **42**, 104—105).—The addition of zinc dust is necessary in the distillation of the ammonia obtained by digesting a nitrogenous substance with sulphuric acid and mercury or with sulphuric acid, phosphoric oxide, and mercury, if potassium sulphide is not added to the sodium hydroxide. If potassium sulphide is used, zinc turnings may be used in place of zinc dust. The results obtained are too low if the zinc is omitted or replaced by aluminium. [See, further, *Ind.*, May.] W. P. S.

Foam Inhibitor in the Van Slyke Amino-nitrogen Method.
H. H. MITCHELL and H. C. ECKSTEIN (*J. Biol. Chem.*, 1918, **33**, 373—375).—The formation of foam during the liberation of nitrogen in the Van Slyke apparatus is prevented by the addition of two or more drops of diphenyl ether, which is readily synthesised from bromobenzene and potassium phenoxide (Ullmann and Sponagel, A., 1905, i, 644). H. W. B.

Alkalimetric Estimation of Phosphorus in Iron and Steel.
NIKOLAUS CZAKO (*Chem. Zeit.*, 1918, **42**, 53—54).—When the yellow ammonium phosphomolybdate precipitate is dissolved in a known excess of sodium hydroxide solution and the excess then titrated with standardised nitric acid, it is recommended that the latter be standardised against potassium hydrogen carbonate. The potassium hydrogen carbonate value of the acid is then multiplied by 0·013481 to obtain the phosphorus value. W. P. S.

Separation of Phosphorus from Vanadium.
ALFRED KROPF (*Chem. Zeit.*, 1917, **41**, 877—878, 890—891).—One gram of the alloy containing phosphorus and vanadium is dissolved in aqua regia, the solution evaporated to dryness, the residue heated gently, then cooled, boiled with the addition of 20 c.c. of hydrochloric acid (D 1·12), diluted to 60 c.c., and filtered to separate silica. The filtrate is treated with 15 c.c. of ammonium citrate solution (prepared by neutralising 1 kilo. of citric acid with ammonia and diluting the solution to 5 litres), and boiled for three minutes to reduce the vanadic acid; after the addition of 30 c.c. of 40% ammonium nitrate solution and 10 c.c. of nitric acid (D 1·18), the phosphoric acid is precipitated with molybdic acid reagent. In the case of ores, the sample is fused with a mixture of sodium and potassium carbonates, or sodium carbonate and potassium nitrate, the mass dissolved in water, filtered, and the filtrate treated as described. If arsenic is present, it may be separated from the vanadium and phosphorus by treatment with hydrogen sulphide, or the phosphorus, together with some of the vanadium, may be precipitated as hydrated aluminium phosphate, and thus separated from the arsenic. W. P. S.

Spectroscopic Detection of Boron.
A. DE GRAMONT (*Compt. rend.*, 1918, **166**, 477—480).—Boron may be readily detected if

present to the extent of 1 in 10,000 by means of the ray $\lambda\,3451\cdot2$ and the doublets $\lambda\,2497\cdot82$ and $2496\cdot87$, shown in the condensed spark spectrum. W. G.

Gasometric Estimation of combined Carbon Dioxide. W. Mestrezat (*Ann. Chim. anal.*, 1918, **23**, 45—47).—A method for the estimation of carbon dioxide in a mixture containing a carbonate and a hypochlorite consists in treating a portion of the sample with sulphuric acid and measuring the volume of the liberated carbon dioxide after the chlorine has been absorbed by oil of turpentine. The estimation is carried out in an ordinary calcimeter, but a tube containing a plug of cotton wool impregnated with oil of turpentine is placed between the reaction flask and the gas-measuring burette. [See, further, *Ind.*, May.] W. P. S.

Estimation of Potassium. Bertram Blount (*Analyst*, 1918, **43**, 117—120).—For the estimation of potassium in siliceous rocks, clays, etc., the material is decomposed with hydrofluoric and sulphuric acids, iron, aluminium, manganese, and calcium are removed from the solution in the usual way, sulphuric acid is separated by treatment with barium hydroxide, and the solution is evaporated to obtain the mixed sodium and potassium chlorides. The quantity of potassium is then estimated by the platinum chloride or perchlorate method. W. P. S.

Calcium in Man. I. Estimation of Calcium in the Blood. W. H. Jansen (*Zeitsch. physiol. Chem.*, 1918, **101**, 176—192).— The blood (10 c.c.) is dried and incinerated. The ash is dissolved in hydrochloric acid, nearly neutralised with ammonia, and the iron and phosphorus removed by boiling with ammonium acetate. The calcium is subsequently precipitated as oxalate from the carefully neutralised filtrate. The precipitate is collected, and, after ignition in the usual way, the residual calcium oxide is estimated by dissolving in a known volume of $N/100$-hydrochloric acid and titrating the excess with alkali or by dissolving in 15 c.c. of $N/100$-hydrochloric acid, adding 25 c.c. of water, 2 c.c. of a 10% potassium iodide solution, 4 drops of a 4% potassium iodate solution, and 2 drops of a 1% starch solution in 20% potassium chloride solution, and then titrating with $N/100$-thiosulphate solution until the blue colour just disappears. H. W. B.

Estimation of Hardness of Water by the Method of Wartha-Pfeiffer. Wagner (*Zeitsch. öffentl. Chem.*, 1917, **23**, 375—379. Compare A., 1914, ii, 490).—This method yields more trustworthy results, particularly in the case of waters containing relatively large quantities of magnesium salts, if the amounts of sodium carbonate and sodium hydroxide in the reagent are increased to $14\cdot5$ grams and $8\cdot01$ grams per litre, respectively. W. P. S.

Estimation of Sulphur and Copper Oxide. C. G. MAIER (*Eng. and Min. J.*, 1918, **105**, 372—373).—For estimating the proportions of copper sulphide and "oxide" or soluble copper in a sample of copper ore, especially for use in flotation processes, the ore is heated with 4% sulphuric acid at 80—90°, the mixture cooled, and clean mercury added and mixed thoroughly with the residue so that it amalgamates with the metallic copper present or reduced from cuprous oxide. The solution is filtered, and the copper determined separately in the filtrate and residue, preferably by the iodide method. The copper in the residue represents the sulphide and that in the solution the "oxide" or soluble copper. [See, further, *Ind.*, May.] W. F. F.

Copper Dicyanodiamide and its Use in Analysis. H. GROSS-MANN and J. MANNHEIM (*Chem. Zeit.*, 1918, **42**, 17—19).—Copper may be precipitated by treating a solution of one of its salts with concentrated dicyanodiamide sulphate solution, rendering the mixture slightly ammoniacal, heating it to boiling, and then adding sodium hydroxide solution until the blue colour changes to reddish-violet. After cooling, the red precipitate is collected, washed with cold water, and dried at 120°; it contains 23·92% of copper. As the precipitate is slightly soluble in water, all the solution used should be concentrated. Nickel may be precipitated in a similar way (compare A., 1907, ii, 819), and the method may be used for the separation of copper and nickel from zinc, aluminium, chromium, arsenic, lead, and antimony. In exceptional cases, where the introduction of alkali into the solution is not desired, dimethylamine may be used in place of sodium hydroxide to precipitate the copper and nickel compounds. W. P. S.

Analysis of Aluminium Alloys. BERNARD COLLITT and WILLIAM REGAN (*J. Soc. Chem. Ind.*, 1918, **37**, 91—94T).— Methods are given for the estimation of copper, iron, nickel, manganese, zinc, magnesium, and silicon in aluminium alloys such as are used in the construction of aircraft and other engines of warfare. In cases where the alloy contains only copper (10 to 15%) and manganese (1%) in addition to aluminium, the copper may be estimated volumetrically by the iodide method; in other alloys it is estimated gravimetrically by precipitation as sulphide by thiosulphate, the sulphide being subsequently ignited and weighed as oxide. The original should be consulted for the details of the methods recommended for the estimation of the other constituents. W. P. S.

Volumetric Estimation of Manganese by means of Sodium Arsenite. FRED IBBOTSON (*Chem. News*, 1918, **117**, 157—158).— When permanganate solution containing nitric acid is titrated with sodium arsenite solution, the latter has a reducing value about 33% in excess of the value it has when used against potassium permanganate solution alone. This appears to be due to the formation of manganic compounds in the presence of nitric acid. [See, further, *Ind.*, May.] W. P. S.

Estimation of Manganese in Aluminium Alloys and Dust.

J. E. CLENNELL (*Eng. and Min. J.*, 1918, **105**, 407—410).—Two methods are described for estimating manganese in dust made from aluminium–manganese alloys.   Several known methods were investigated, but the following much simpler methods are preferred : 1 Gram of the sample is carefully heated with 50 c.c. of 50% nitric acid, and finally boiled to expel oxides of nitrogen.   The solution is filtered, the residue washed, placed in a nickel crucible, dried, ignited, and the ash covered with sodium peroxide.   The mixture is fused, and the product dissolved in water and added to the previous nitric acid solution.   The mixture is boiled, and about 1 c.c. of standard silver nitrate solution added to remove chlorides. 0·1 Gram of lead peroxide is added for each estimated 0·1 gram of manganese present, the mixture boiled, cooled, made up to 100 c.c., and filtered.   Fifty c.c. of the filtrate are titrated with standard sodium arsenite which has been standardised against a manganese salt.   Another method is described in which ammonium persulphate is substituted for lead peroxide, but this was not so trustworthy owing to the variability in the quality of the persulphate.   [For details, see *Ind.*, May.]   W. F. F.

Gravimetric Estimation of Chromates and Dichromates.

L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 46—48).— I. *As Barium Chromate.*—One hundred c.c. of a neutral solution containing about 0·2% of an alkali chromate are treated with 1 c.c. of $N/10$-acetic acid and 1 gram of sodium chloride, heated to boiling, and 5 c.c. of 10% barium chloride are added slowly while the mixture is stirred.   The mixture is kept boiling for three minutes, then cooled, and, after eighteen hours, the precipitate is collected, washed with 50 c.c. of cold water, dried at 132°, and weighed. When the precipitate weighs less than 0·1 gram, the weight found is about 1 mg. too low.   If the precipitate is ignited before being weighed, it loses 0·25% in weight.   The presence of ammonium, potassium, magnesium, and calcium chlorides does not interfere, but nitrates, chlorates, and acetates cause the results to be too high.   Dichromates are estimated in a similar way after their solution has been boiled with the addition of calcium carbonate and filtered.   II. *As Silver Chromate.*—This method must be used if the chromate solution contains sulphate; in any case, it is more trustworthy than the barium chromate method, but cannot be used in the presence of chlorides.   One hundred c.c. of the chromate solution (or dichromate solution after treatment with calcium carbonate) are boiled and 5 c.c. of 10% silver nitrate solution are added.   After eighteen hours, the precipitate is collected, washed with 50 c.c. of water saturated previously with silver chromate, dried at 132°, and weighed.   The results are not affected by the presence of nitrates, chlorates, or acetates, but sulphates cause the results to be too high.   W. P. S.

Colorimetric Estimation of Tungsten.

A. TRAVERS (*Compt. rend.*, 1918, **166**, 416).—For this method, using titanous chloride

(compare A., 1917, ii, 545), the tungsten solution should not contain more than 0·1 gram of the metal in 100 c.c., and the acidity of the solution should not exceed $N/10$. The estimation cannot be performed in the presence of vanadium, phosphorus, or molybdenum. W. G.

[**Estimation of Uranous Salts in Presence of Formic Acid.**] E. C. HATT (*Zeitsch. physikal. Chem.*, 1918, **92**, 513—562).—Compare this vol., ii, 144.

Oxidimetric Estimation of Thorium Precipitated as the Oxalate. F. A. GOOCH and MATSUSUKE KOBAYASHI (*Amer. J. Sci.*, 1918, [iv], **45**, 227—230).—The following conditions are given for the estimation of thorium by titration, with permanganate, of its oxalate, or of the excess of oxalic acid used for the precipitation. The oxalate is precipitated by adding the thorium solution to an excess of cold oxalic acid solution; the reverse procedure is less trustworthy owing to the formation of basic compounds, especially in hot solutions. After thirty minutes, the precipitate is collected on an asbestos filter, washed with cold water containing one drop of concentrated sulphuric acid in each 25 c.c., the filter and precipitate are then transferred to a beaker containing 100 c.c. of water, the mixture is heated at 85°, 5 c.c. of sulphuric acid (1:1) are added, and the solution is titrated with $N/10$-permanganate solution until the greater part of the oxalate has been oxidised; the solution is then heated again at 85° and the titration completed. If a known excess of oxalic acid has been used, the filtrate from the oxalate precipitate may be heated at 85°, acidified with sulphuric acid, and titrated with permanganate. In this case, there is no need to reheat the titration mixture. The precipitated thorium oxalate has the composition $Th(C_2O_4)_2$. W. P. S.

The Estimation of Tantalum in its Alloys with Iron. A. TRAVERS (*Compt. rend.*, 1918, **166**, 494—495).—In the estimation of tantalum, the precipitate of tantalic acid usually contains some silica, and if this is removed by means of hydrofluoric acid, some of the tantalic acid is also lost. The tantalic acid may, however, be volatilised in a current of hydrogen chloride at 900°. The silica which is left is weighed, and the weight deducted from that of the original precipitate.

For details of application to steels, etc., see *Ind.*, 244A. W. G.

Detection and Estimation of Methyl Alcohol, its Presence in Various Foodstuffs, and the Behaviour of Foodstuffs containing Methyl Alcohol in the Organism. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **85**, 45—117. Compare A., 1917, i, 616).—A detailed account is given of the modification of Denigès's method for estimating methyl alcohol. The essential process consists in the oxidation of the liquid (which generally con-

tains ethyl alcohol) with permanganate, and the colorimetric estimation of the formaldehyde thus obtained by oxidation under standard conditions by magenta-sulphurous acid solutions.

A new method is also given for determining the presence of methyl alcohol when it is only present in small quantities. The essential process consists in the fractional separation of the mixed methyl and ethyl alcohols by potassium carbonate. The alcohol separated first by incomplete saturation with the carbonate contains scarcely any methyl alcohol. After separation of fractions containing only minute amounts of methyl alcohol, the residue is distilled. The distillate is fractionated, and the first fractions are redistilled. These fractions are again redistilled, the earlier fractions only being retained. A fraction is finally obtained which is rich in methyl alcohol, and this, after drying over calcium oxide, is converted into iodides, from which a fraction rich in methyl iodide can be separated.

It is shown that the methyl alcohol in certain spirits is derived chiefly from the pectin substances, from which 10—11% of methyl alcohol can be separated by treating with dilute sodium hydroxide.

The lignins of wood also yield methyl alcohol, but this is not eliminated so readily as that of pectins. It can be obtained in various fractions by treating the wood first with sodium hydroxide to eliminate the pectin alcohol, and then with graded strengths of sulphuric acid. Each filtrate obtained in this way is then treated with 70% sulphuric acid, and the methyl alcohol in the distillate is estimated, as well as the methyl alcohol in the distillate, before treatment with the 70% acid.

The methyl alcohol of the pectins and lignins was determined in a large number of different kinds of woods, etc.

An investigation was also made of the effect of ingestion of substances containing pectins. The ingestion of pectin-containing substances caused a small increase in the excretion of methyl alcohol in the urine, which was much more marked when ethyl alcohol was ingested at the same time. It was suggested that certain symptoms found in the drinkers of spirits may be due to the methyl alcohol contained therein. [See also *Ind.*, May.]   S. B. S.

Estimation of Glycerol by Wagenaar's Method. J. H. M· BECKERS and I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 272—281).—Wagenaar's method of estimating glycerol (A., 1911, ii, 663) gives results dependent on the composition and temperature of the liquid. Methyl alcohol is without influence on the reaction, but the presence of ethyl alcohol, haloids, nitrates, and to a less degree sulphates, is deleterious. With fats, it is best to saponify with methyl-alcoholic potash and remove the fatty acids with the minimum quantity of sulphuric acid.   A. J. W.

Estimation of the Amount of Water in Glycerol. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 304—307).—An account of a method of estimating the percentage of water in glycerol by observing the temperature range of complete miscibility of mixtures

of the sample and aniline. A table showing the corresponding percentages of water is given. A. J. W.

Methylene-blue a Sensitive Reagent for the Detection of Picric Acid in Urine. ROZIER (*Bull. Sci. Pharmacol.*, 1917; from *Ann. Chim. anal.*, 1918, **23**, 63).—The urine is treated with normal lead acetate and filtered; 4 c.c. of the filtrate are placed in a test-tube, one drop of 0·5% methylene-blue solution is added, and the mixture is shaken with 1 c.c. of chloroform. After separation, the chloroform layer has a green colour if picric acid or picramic acid is present in the urine; in their absence, the chloroform is coloured blue. The test will detect the presence of 2 mg. of picric acid per litre of urine. W. P. S.

Colorimetric Estimation of Picric Acid and its Derivatives in Body Fluids. X. LAPORTE (*Bull. Soc. Pharm. Bordeaux*, 1917, No. 3; from *Ann. Chim. anal.*, 1918, **23**, 64).—A definite volume of the fluid (which should be diluted or concentrated so that it contains about 0·01 gram of picric acid per litre) is neutralised and treated with 0·5 c.c. of ferrous sulphate–tartaric acid reagent (compare A., 1917, ii, 158) and 1·5 c.c. of ammonia; these quantities of reagents are required for each 10 c.c. of the sample. The coloration obtained is compared with that produced by a known amount of picric acid under the same conditions. W. P. S.

Estimation of Cholesterol. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1918, **101**, 89—98).—The author finds that the method described by Windaus (A., 1909, i, 172) for recovering the cholesterol or similar component from the digitonin–cholesterol complex is unsatisfactory. By the following procedure, a quantitative separation is effected. About 0·5 gram of the anhydrous complex is weighed out and boiled with 5 c.c. of acetic anhydride for twenty to thirty minutes under a reflux condenser. The hot liquid is poured into about 80 c.c. of water. After the product of the reaction has solidified, it is collected, washed, and dried in a vacuum. It is now removed as completely as possible from the filter paper, transferred to a small flask, dissolved in 10 c.c. of 90% alcohol, and mixed with 10 c.c. of 1% aqueous sodium hydroxide. The resulting emulsion is boiled for two and a-half to three minutes, cooled, diluted with water, acidified, and extracted with ether. The cholesteryl acetate dissolves in the ether, whilst the digitonin remains in the dilute alcohol. After evaporation of the ether, the cholesteryl acetate is hydrolysed with alcoholic potassium hydroxide, and the free cholesterol or similar compound extracted by ether, weighed, and subsequently identified in the usual way. H. W. B.

Detection of Acetone in Urine. HANS TRUNKEL (*Pharm. Zeit.*, 1918, **63**, 104—105).—Legal's nitroprusside test is trustworthy and gives the best results when applied as a ring test. Two

c.c. of the urine are mixed with ten drops of 20% sodium nitroprusside solution and 1 c.c. of acetic acid, and 2 c.c. of ammonia are poured on the surface of the mixture; if acetone is present, a violet-red zone appears at the junction of the two liquids. Reichardt's test (A., 1916, ii, 119), in which the acetic acid of the Legal test is replaced by ammonium chloride, is less trustworthy, since a feeble coloration is obtained in the absence of acetone. It is not necessary for the nitroprusside solution employed to be freshly prepared; the solution, if made with the pure salt, keeps almost indefinitely.   W. P. S.

Estimation of Pyridine Bases in Ammonia and its Salts. T. F. HARVEY and C. F. SPARKS (*J. Soc. Chem. Ind.*, 1918, **37**, 41—43T).—The pyridine is precipitated as periodide from a sulphuric acid solution of the sample (ammonia, ammonium carbonate, or other salt) in the presence of sodium chloride, the periodide is converted into sulphate, and the latter titrated with alkali solution. When sufficient sodium chloride is added, 1 mg. of pyridine in 200 c.c. of $N/2$-sulphuric acid is precipitated completely as periodide. The method in detail is as follows: Fifty c.c. of the sample of ammonia (D about 0·885) is treated, in a separating funnel provided with a plug of cotton wool above the tap, with 100 c.c. of $10N$-sulphuric acid, the mixture being cooled during the addition of the acid. Fifty grams of sodium chloride are then dissolved in the mixture, and 10 c.c. of iodine solution (iodine, 13 grams, and potassium iodide, 13 grams, per 100 c.c.) are added. The mixture is shaken, and, after fifteen minutes, the liquid portion is forced through the cotton wool filter; the precipitate is washed with 20 c.c. of a mixture of $10N$-sulphuric acid, 10 c.c., water, 190 c.c., and iodine solution (see above), 10 c.c., then decomposed by a slight excess of saturated thiosulphate solution, diluted to about 20 c.c., and neutralised with $N/1$-sodium hydroxide solution, using methyl-orange as indicator. Phenolphthalein is then added, and the pyridine sulphate titrated with $N/10$-sodium hydroxide solution; 1 c.c. of the latter is equivalent to 0·0079 gram of pyridine. The solution employed for washing the periodide precipitate should be made about eighteen hours before using and be filtered if necessary.   W. P. S.

Colour Reactions in the Chemico-legal Examination of Bloodstains. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quim. Argentina*, 1917, **5**, 177—184).—A review of the various colour tests proposed for the identification of bloodstains.   A. J. W.

General and Physical Chemistry.

The Optics of Disperse Systems. I. I. LIFSCHITZ (*Kolloid Zeitsch.*, 1918, **22**, 53—57).—A general discussion of the optical properties of disperse systems, including the absorptive power, the refractivity, and the rotatory power of optically active colloids.
H. M. D.

The Relation between the Degree of Supersaturation, the Refractive Index and the Temperature of Sugar Solutions. E. V. MILLER and F. P. WORLEY (*J. Soc. Chem. Ind.*, 1918, **37**, 98—103T).—Measurements have been made of the refractive index of supersaturated solutions of sucrose with the object of determining the influence of temperature and concentration on the refractive index between 30° and 75° and between 72% and 81% of sucrose, which range of concentration is of technical importance. The results obtained show that the refractive index, in its dependence on the temperature t and the percentage concentration p, can be satisfactorily represented by the equation $r = 1.28534 - 0.0001241t + (0.00263 - 0.000001267t)p$. This equation may be written in an alternative form, in which r is represented as a function of the temperature and the degree of supersaturation s, the relation between p and s being given by $p = 100(S + s)/100 + S + s$, in which S represents the number of parts of sucrose per 100 of water in the saturated solution. A table is given showing the values of the refractive indices of solutions for $s = 0$ to $s = 110$, and for temperatures ranging from 43.3° to 76.6°. H. M. D.

The Arc Spectrum of Europium and a New Element, Eurosamarium, between Europium and Samarium. JOSEF MARIA EDER (*Sitzungsber. K.K. Akad. Wiss. Wien*, 1917, IIA, **126**, 473—531; from *Chem. Zentr.*, 1918, i, 70—71).—Europium imparts a fine red colour to the electric arc, and its characteristic groups of lines are very bright and easily distinguished. The author has examined the photograph of the spectrum of one of Urbain's preparations, which proved to be remarkably pure, and has also tested two samples supplied by Auer, the one being a europium fraction related to gadolinium and the other a specimen akin to samarium. In these, he has measured 1171 europium lines between 7370 and 2373. The lines which were obtained with the material quite free from samarium included some which are ascribed to a new element, *eurosamarium*, and these are tabulated in the original. J. C. W.

Atomic Weights of the Elements in Nebulæ. J. W. NICHOLSON (*Month. Not. Roy. Astr. Soc.*, 1918, **78**, 349—362).— A theoretical paper in which equations are derived for the periods

of vibration of atoms with a single ring of electrons. These equations, in combination with the wave-lengths of the principal lines in the spectrum of nebulium, give for m/M the value $0·000415$, in which m is the mass of an electron and M the mass of the atom. Assuming that for hydrogen $m/H = 0·000545$, the atomic weight of nebulium is found to be $1·31$, with a possible error of one unit in the second decimal place.   H. M. D.

The Shifting of Radioactive Equilibria under the Influence of Fluorescein. H. ZWAARDEMAKER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 768—772. Compare A., 1917, i, 241).—The antagonism between potassium and uranium in their influence on the pulsation of the frog's heart is found to be appreciably affected by the addition of fluorescein in the sense that a larger quantity of potassium is required to antagonise a given quantity of uranium if fluorescein is added to the solution. The displacement produced by fluorescein is in the same direction as that which, according to observations on summer and winter frogs, is produced by a rise of temperature.   H. M. D.

Radioactivity of Waters of the Mountainous Region of Northern Luzon (Philippines). GEORGE W. HEISE (*Philippine J. Sci.*, 1917, **12**, [A], 293—307).—In continuation of previous work (Wright and Heise, A., 1917, ii, 560), the author has examined the waters of a number of springs and wells in northern Luzon. The region shows evidence of recent vulcanism. The data are not yet numerous enough to warrant general conclusions, but they do not confirm the usual observation that radioactivity is most common among waters from volcanic regions, or at least among thermal springs. Of the numerous salt springs and hot springs examined, none showed high radioactivity. The most active waters were rich in calcium and magnesium, indicating an origin in calcareous material. High activity was found only in waters from a small district (Ifugao), and was probably due to the presence of local deposits of radioactive material.   J. H. L.

Constancy in the Radioactivity of certain Philippine Waters. GEORGE W. HEISE (*Philippine J. Sci.*, 1917, **12**, [A], 309—311).—Measurements of the radioactivity of the water of a Philippine spring at different periods of the year showed no appreciable changes, in spite of great variations in the rate of flow of the spring. The composition of the water is substantially the same as in 1890.   J. H. L.

Extrapolation of Conductivity Data to Zero Concentration. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1918, **40**, 622—623).—Polemical, in which the author claims priority over Washburn (this vol., ii, 55) in the method employed by the latter for the calculation of the zero concentration values of conductivity data. [See T., 1912, **101**, 1279, 1291.]   J. F. S.

Electrolytic Dissociation in Solvents with Low Dielectric Constants. V. A. PLOTNIKOV (*Reprint*).—From theoretical considerations and the results of conductivity measurements on various solutions, the following conclusions are drawn. Solvents with low dielectric constants are capable of forming solutions showing high electrical conductivity. The conductivity of a solution depends to as great an extent on the solute as on the solvent; these two must be in peculiar electrochemical correspondence in order that they may yield a conducting solution. The phenomenon of electrical conductivity in a solution cannot be explained by any definite property of the solvent conditioning its dissociating capacity; electrochemical investigation of a solution has to deal with a conducting "couple." Electrochemical correspondence is explained as due to the resonance of the movement of the solvent molecules with the ionic vibrations of the electrolyte.   T. H. P.

Electrochemical Potential and the Periodic Law. J. C. THOMLINSON (*Chem. News*, 1918, **117**, 176).—The relation between electrochemical potential and the position of the elements in the periodic system is demonstrated by means of a curve. In this curve, starting with the most electropositive element, cæsium, the elements follow the order cæsium to lithium (as in group I), barium to magnesium (as in group II), aluminium, chromium, manganese, zinc, cadmium, iron, cobalt, nickel, hydrogen. The non-metals then continue the curve, and these, after silicon, carbon, and boron, all occupy positions in the upper right-hand corner of the periodic table.   J. F. S.

The Passivity of Chromium. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 812—823).—The values recorded in the literature for the potential of the chromium electrode are very divergent, and this is supposed to be connected with the tendency of the metal to assume the passive condition. Electrodes were prepared from chromium obtained by Goldschmidt's method, by the electrolysis of solutions containing a mixture of chromic sulphate and chromic acid, and by the electrolysis of solutions of chromic chloride. These were brought into contact with a 0·3 molar solution of chromous sulphate and combined with a normal calomel electrode.

The results obtained indicate that the potential of chromium in contact with chromous sulphate solution is about $-0·75$ volt, or $-0·47$ volt when referred to the hydrogen electrode. This active potential value is only attained when hydrogen is present in the metal in sufficient quantity. The hydrogen appears to act as a catalyst in promoting the establishment of the electrode equilibrium.   H. M. D.

Potential Measurements on the Copper-Nickel Series of Alloys and some observations on Brasses. NEWELL T. GORDON and DONALD P. SMITH (*J. Physical Chem.*, 1918, **22**, 194—215).—A study of the factors affecting the potential differ-

ence between a binary (solid) alloy and an electrolyte containing the corresponding ions (see A., 1916, ii, 214). With copper–zinc alloys, no treatment employed was sufficient to ensure reproducibility or constancy in the "steady" potential finally attained, but copper–nickel alloys are shown to be very regular in electrochemical conduct, and the potential values are reproducible and constant for many hours.

Six ingots of copper–nickel alloys, containing 6·8, 10·9, 65·5, 74·3, 83·4, and 94·7% of Cu were carefully prepared, and a small test-piece $2 \times 2 \times 2\frac{1}{2}$ mm. cut from each, the end surface of each bar forming a portion of a horizontal plane passing through the middle of the ingot, and this was the part exposed afterwards to the electrolyte. Each piece was annealed in an atmosphere of nitrogen, the first two at 218° and the others at 600°. The electrolytes employed were all $N/1$-solutions of copper and nickel sulphates combined, and some contained in addition $N/1$-sodium sulphate. All potentials were measured at 25° against a normal calomel electrode by means of a potentiometer and a galvanometer. For some time after immersion the potential changes rapidly, but after some hours a steady value is reached, which afterwards remains constant within 3 millivolts during the period of observation. It is found that carefully annealed specimens give the most constant results, and although there are no regular differences between the steady potentials of surfaces annealed and treated with emery, yet the latter exhibit greater accidental variations. Polished surfaces have a greater tendency to give ions to the solution. With alloys from a given ingot, and also with ingots of a similar composition, it was found that the steady potential is definitely determined by the composition of the electrolyte. The potential differences exhibited are expressible by a relation which is linear both with respect to alloy composition and to the logarithm of electrolyte composition.

It is shown that copper sulphate concentration may be employed without any sacrifice of accuracy in the representation of the empirical results in place of the cupric ion concentration required by Nernst's thermodynamic theory, provided the constants of the equation are altered.   B. N.

The Lead Electrode. II. FREDERICK H. GETMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 611—619).—Since the publication of the previous paper (A., 1916, ii, 287), the question of the possible allotropy of lead has arisen. The present work was undertaken to furnish an answer to this question. The *E.M.F.* of cells of the type $Pb \mid 0·1M KCl$ sat. with $PbCl_2 \parallel 0·1M KCl, Hg_2Cl_2 \mid Hg$ has been measured at 25°, using lead electrodes from various sources and treated in different ways. It is shown that the value of the *E.M.F.* obtained with different specimens of lead cast into sticks, with electrolytically deposited lead, and with lead amalgams, was the same in all cases. The normal electrode potential of lead was calculated from the results to be 0·4121 volt referred to the

N-calomel electrode and 0·1293 volt against the N-hydrogen electrode. The values of the $E.M.F.$ of cells containing electrodes which had been immersed for varying periods of time in Heller's solution (400 grams lead nitrate, 1000 c.c. water, and 100 c.c. nitric acid [D 1·16]) were found to be about 8 millivolts higher than the values obtained with cells containing electrodes which had not been subjected to this treatment. The temperature coefficient of the cell was found to be 0·00022. The heat of the reaction $Pb + Hg_2Cl_2 = PbCl_2 + 2Hg$ was calculated, and found to be 21,840 cal., and the heat of formation 84,440 cal. The heat of reaction U_0 and the maximum work $A_{234°}$ were calculated by means of the Nernst-Lindemann equation, and the value of the $E.M.F.$ at $234°$ A computed. The values $U_0 = 24.035$ cal., $A_{234°} = 24,041$ cal., were obtained, and the value of the $E.M.F.$ was in close agreement with the experimental value.   J. F. S.

The Quantum Theory of Paramagnetism. FRITZ REICHE (*Ann. Physik*, 1917, [iv], **54**, 401—436).—A mathematical paper in which the quantum hypothesis is applied in the development of a theory of paramagnetism. The formula derived for the relation between the magnetic susceptibility and the temperature is tested by reference to the available data for ferrous sulphate and manganous sulphate, and found to be quite satisfactory.   H. M. D.

Investigations on the Thermal Conductivity of Gases. I. and II. SOPHUS WEBER (*Ann. Physik*, 1917, [iv], **54,** 325—356, 437—462).—The sources of error involved in the determination of the thermal conductivity of gases by Schleiermacher's method are subjected to a critical analysis, and a modified form of apparatus is described in which the errors due to convection are greatly reduced. With this improved form of apparatus, measurements have been made of the thermal conductivity of a number of gases.

The following values are recorded: hydrogen, $4·165 \times 10^{-4}$; neon, $1·089 \times 10^{-4}$; helium, $3·438 \times 10^{-4}$; argon, $3·850 \times 10^{-5}$; nitrogen, $5·660 \times 10^{-5}$; oxygen, $5·768 \times 10^{-5}$; methane, $7·200 \times 10^{-5}$; carbon dioxide, $3·393 \times 10^{-5}$; nitrous oxide, $3·530 \times 10^{-5}$. The results are discussed in reference to certain aspects of the theory of the conductivity of gases.   H. M. D.

The Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 750—767).— A theoretical paper in which the author discusses the influence of temperature and volume on the constants a and b of the van der Waals's equation. It has been suggested by van der Waals that a varies with the volume if the temperature is lower than the critical temperature, but the author's arguments lead to the conclusion that a depends only on the temperature, whether this is above or below the critical temperature. On the other hand, b appears to be a function of both temperature and volume.
          H. M. D.

The Saturated Vapour Pressures of Triatomic Liquids.
E. ARIÈS (*Compt. rend.*, 1918, **166**, 668—672. Compare this vol.,
ii, 61).—Using the known physical constants for carbon
dioxide, the author deduces the formula $\Pi = \tau^{14/5} Z/x$, where
$x = [1 + (1 - \tau)(0.88 - \tau)/0.40(\tau^2 + 1)]\tau^{9/5}$ for the saturated vapour
pressures of triatomic liquids. The observed results are in fairly
close agreement with those calculated by this formula in the cases
of sulphur dioxide and nitrous oxide, but this is not true for
hydrogen sulphide and water.   W. G.

The Adsorption of Sodium Gold Chloride by Charcoal.
The Estimation of Gold in Sea-water.   HELLMUTH KOCH
(*Kolloid Zeitsch.*, 1918, **22**, 1—22).—The adsorption of gold from
very dilute solutions of gold chloride in 3% sodium chloride by
various forms of carbon has been examined with a view to the
application of the adsorption process in the estimation of gold
in sea-water. Measurements of the rate of the adsorption show
that this takes place fairly rapidly, but the attainment of a con-
dition of equilibrium is prevented by the fact that the adsorbed
gold salt is slowly reduced, and in consequence of this there is a
continuous fall in the concentration of the gold in the aqueous
solution. The concentration time curve consists accordingly of
two branches of very different slopes, the intersection of which
affords a sufficiently accurate measure of the adsorption effect.

The results obtained for solutions of varying concentration are
satisfactorily represented by means of the ordinary adsorption
equation. Finely divided wood charcoal was found to be the most
satisfactory adsorbent, and this material was used in experiments
on sea-water, three samples of which gave results indicating the
presence of 2·5 to 4 mg. of gold per cubic metre. These values for
the quantity of gold in sea-water are in agreement with the results
obtained by some earlier observers, although much larger values
have been recorded. The literature of the subject is discussed in
detail. [Compare *J. Soc. Chem. Ind.*, June.]   H. M. D.

Influence of Neutral Salts on the Dissociation Constants
of Indicators. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, **15**,
394—400).—The dissociation constants of phenol, aniline, and
colorimetric indicators are increased by addition of neutral salts.
This fact explains the development of the alkaline tint on addition
of a neutral salt to an acid indicator, and the corresponding
development of the acid tint of an alkaline indicator. The effect
is very marked in the case of azolitmin.   A. J. W.

[**Diffusion of Gases through Indiarubber.**]   SIR JAMES
DEWAR (*Proc. Roy. Inst.*, 1918, **21**, 813—826).—An appendix to
a lecture on " Problems of Hydrogen and the Rare Gases " (compare
ibid., 543). An account is given of apparatus which has been
used by the author in the investigation of the diffusion of gases
through thin rubber membranes at varying pressures and
temperatures.

With a membrane about 0·01 mm. thick, the rates observed for different gases, at atmospheric pressure and 15°, in c.c. per day per cm.² were: air, 2·0; nitrogen, 1·38; carbon monoxide, 1·88; helium, 3·5; argon, 2·56; oxygen, 4·0; hydrogen, 11·2; carbon dioxide, 28·0. The order in which the gases are arranged according to their diffusibility does not appear to be directly related to any chemical or physical property of the gases concerned.

The rate of diffusion increases rapidly with rise of temperature, and when the logarithm of the rate is plotted against the temperature, straight line graphs are obtained. These lines all show a distinct break at 0°, which suggests that water is in some way involved. In the case of carbon dioxide, a much more pronounced break is found at −37°.

The composition of the gaseous mixture resulting from the diffusion of air through rubber has been examined by ordinary chemical analysis and also by the spectroscopic investigation of the residue obtained after subjecting the mixture to the action of charcoal cooled in liquid air. By this means, it has been found that the hydrogen and helium in air diffuse at nearly the same rate, whilst the rates of diffusion of helium and neon are as 9 to 1.

Observations were also made on the diffusion of gases through rubber membranes immersed in different liquids, such as water, salt solutions, ethyl alcohol, and glycerol.   H. M. D.

Diffusion in Anisotropic Liquids. THE. SVEDBERG (*Kolloid Zeitsch.*, 1918, **22**, 68—71).—In view of the necessity of maintaining a constant temperature in the diffusion experiments, the author has made use of an equimolecular mixture of *p*-azoxyanisole and *p*-azoxyphenetole. This mixture, which melts at 95° and becomes isotropic at 150°, is convenient for the observations in that the diffusion measurements may be made at 100°. The rate of diffusion of *m*-nitrophenol in the anisotropic liquid was measured (*a*) in the absence of an external magnetic field, (*b*) in a longitudinal magnetic field, and (*c*) in a transverse magnetic field. The results obtained show that the rate of diffusion is increased by the application of the longitudinal field and diminished when the direction of the field is transverse to that in which diffusion takes place.   H. M. D.

Kinetic Theory of Osmotic Pressure and of Raoult's Law. II. G. JÄGER (*Ann. Physik*, 1917, [iv], **54**, 463−480. Compare A., 1913, ii, 762).—A theoretical paper devoted to the consideration of the kinetic interpretation of osmotic pressure and of Raoult's vapour pressure law.   H. M. D.

Manifestation of Osmotic Pressure with Membranes of Chemically Inert Materials. S. L. BIGELOW and C. S. ROBINSON (*J. Physical Chem.*, 1918, **22**, 153—183).—A method and apparatus have been devised for the study of osmotic phenomena with membranes of powdered materials, such as silica,

amorphous carbon, graphite, metallic copper, gold, and silver. The membranes were prepared by alternately pressing the purified material under a high pressure and clogging the pores by sucking a fine material in suspension through the membranes. Thus, in the case of pure silica, a pressure of 350 kilos. per cm. was used, and the largest pores in two membranes were reduced to 1·4823 and 0·3488 microns respectively. Amorphous carbon was prepared by ignition of a pure sucrose, compressed, and clogged as above, but the pore diameters in this, and in flaky graphite washed with acid and similarly treated, had to be considerably reduced to produce osmosis. Reduced copper and silver powders had to be pressed for several days at 350—450 kilos. per cm. to reduce the diameters, and the results show generally that the magnitude of osmotic effects increases with a decrease in the diameters of the pores of the membrane. It appears to be fairly obvious that the various examples of osmosis are not due to one but to a variety of causes, and according to the various theories osmosis may take place (1) through capillary spaces in the membrane, (2) by solution of the solvent in the membrane, (3) by the formation of a labile chemical compound between the membrane and the solvent. The present work has demonstrated that osmotic pressure can be produced through the agency of capillary forces alone, without the aid of solution processes or chemical reactions.

B. N.

Theory of Solutions. Solubility Studies in Ternary Mixtures of Liquids. John Holmes (T., 1918, **113**, 263—275, Compare T., 1913, **103**, 2147).—In the further investigation of the theory that the miscibility of liquids is determined by the possibility of the close-packing of the different kinds of molecules, and is therefore dependent on the relative molecular radii, the author has examined a number of three-component systems.

The theory indicates that these liquids should be miscible in all proportions if the molecular radii are equal. If the molecules are of different sizes, the dimensions of the interspaces will decrease as the ratios between the several radii increase until a point is reached at which close packing is a maximum. In the case of an equimolecular mixture this occurs when the radii are as 1·682 : 1·466 : 1. If the respective ratios are greater than these limiting values which correspond with the border line between complete and partial miscibility, separate layers are formed.

So long as the radial ratio of the two smaller molecules is not greater than 1·618 and the corresponding ratio for the extreme molecules exceeds 1·682, but is less than $(1·618)^2$, the mixture should separate into two layers only. If the ratios are greater than these values, three separate layers are to be expected.

In the expectation that the higher paraffin hydrocarbons would afford liquids for which the molecular radii compared with water are greater than $(1·618)^2$, the author has examined the miscibility of various binary mixtures of petroleum and water with a third

substance. Three-layer systems were obtained with aniline, phenol, nicotine, and nitrobenzene, and the behaviour of these mixtures is described.

Three liquid layers were also found in the case of mixtures of petroleum, glycerol, and nitrobenzene. H. M. D.

Condition of Substances in Solution in Absolute Sulphuric Acid. VIII. G. ODDO [with A. CASALINO]. (*Gazzetta*, 1918, **48**, i, 17—44).—The author uses the results of his previous measurements, some of which have now been repeated and confirmed, to refute the criticisms of Hantzsch (*ibid.*, 1911, **41**, i, 645). T. H. P.

Flocculation. SPENCER UMFREVILLE PICKERING (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 315—325).—Experiments have been made to determine the effect of freezing on the sedimentation of certain voluminous precipitates, such as basic copper sulphate, cupric hydroxide, ferric hydroxide, and aluminium hydroxide, and also on clay and kaolin. In all cases, sedimentation takes place more rapidly after freezing, and the volume of the sediment from the liquids which have been frozen is considerably smaller than that from liquids which have not been subjected to this treatment. The shrinkage observed varies from 40 to 90%, and is probably due to dehydration.

The flocculation of suspensions of kaolin on the addition of various substances has been examined, with results which show that the process is accompanied by a considerable increase in the volume of the particles. The increase in the volume of the sediment when acids or salts are used as the flocculating agents is closely related to the quantity of kaolin remaining in suspension, the latter becoming nil when the former reaches a maximum. When the added substance produces no flocculation, there is no increase in the volume of the sediment. In explanation of these relations, it is suggested that the kaolin combines with the flocculant. H. M. D.

Jellies Formed by Dyes. R. HALLER (*Kolloid Zeitsch.*, 1918, **22**, 49—57).—It has been observed that hot concentrated solutions of substantive dyes produce jellies when the solutions are allowed to cool. Experiments made with benzopurpurin 4 B and chrysophenin B show that the formation of these jellies is dependent on the presence of small quantities of electrolytes in the dyes. If a 1% solution of either of the dyes is subjected to dialysis, the electrolytes are removed and the contents of the dialyser separate into two parts, one of which is liquid and the other of gelatinous consistency. The latter does not dissolve even when heated to 100°, and it seems probable that the colloidal dye has been rendered insoluble by the removal of the electrolytes. If the dialysed substance is dried and powdered, the product is markedly different from the original dye in its small solubility

in water. The purified substance dissolves quite readily, however, if sodium chloride is added to the water.

The structure of the benzopurpurin 4 B jellies has been examined and found to be very similar to that of the soap jellies described by Zsigmondy and Bachmann (A., 1912, ii, 1149). [See, further, *J. Soc. Chem. Ind.*, June.] H. M. D.

The Quaternary System, $AgNO_3$–$NH_4 \cdot NO_3$–$Ba(NO_3)_2$–Water at 30°. (Miss) W. C. DE BAAT (*Chem. Weekblad*, 1918, **15**, 463—468).—An application of Schreinemakers's graphic method to aqueous solutions of the nitrates of silver, ammonium, and barium at 30°. A. J. W.

A Method of Obtaining General Reaction-Velocity Curves for Complete Homogeneous Gas Reactions at Constant Pressure. GEORGE W. TODD (*Phil. Mag.*, 1918, [vi], **35**, 435—444. Compare this vol., ii, 102).—The method previously described for the derivation of curves representing the progress of homogeneous reactions at constant volume has been extended to the case of binary gas reactions taking place at constant pressure.

For a bimolecular reaction of the type $A + B \longrightarrow$, in which a gram mols. of A react with b gram mols. of B, v is the total volume of reactants and resultants, and x the number of gram mols. transformed in time t, the equation for the velocity of the reaction when B is in excess may be written in the form $dX/dt = k \cdot a/v_0 \cdot (1-X)(p-X)$, where $X = x/a$, $p = b/a$, and v_0 is the original value of v. Since the right-hand side of this equation does not involve the constant, which, in a particular case, is determined by the ratio between the numbers of mols. of reactants and resultants, it follows that the general curves previously given will be applicable to the case of bimolecular reactions at constant pressure as well as at constant volume.

Termolecular reactions of the type $2A + B \longrightarrow$ with A and B in excess are also considered, and general equations devised for these. The curves which are plotted from these equations show the change of X with t for different values of $p = b/a$, and two sets of diagrams are given corresponding with the case where the volume of the resultants is $2/3$ and $1/3$ respectively of the volume of the reactants. This volume change is expressed in the general equation for the velocity by means of a quantity α, in terms of which, if B is present in excess, $v = v_0\{3a(1 + \alpha X) + (b-a)\}/3a + (b-a)$, and if A is present in excess, $v = v_0\{3b(1 + \alpha X) + 2(a-b)\}/3b + 2(a-b)$. H. M. D.

Periodic System of the Elements. P. V. WELLS (*J. Washington Acad. Sci.*, 1918, **8**, 232—234).—The author has redrawn the spiral periodic table of Stoney and others as revised by Harkins and Hall, and has given it a period of 8 instead of 16. The distance from the centre of the spiral to an

element represents the atomic weight, and the elements are arranged in angular order of atomic number, each group being placed radially with the sub-groups slightly displaced. The metals of positive valence are sharply separated from the non-metals of negative valence. The proposed arrangement is much simpler than the double helix and has all its advantages; it overcomes the artificiality of the 16-period table and brings the main groups and sub-groups together. The new table is particularly adapted to illustrating the electron theory. The possibility of two forms of neon is indicated. A. B. S.

Characteristic Frequency and Atomic Number. H. STANLEY ALLEN (*Proc. Roy. Soc.*, 1917, [*A*], **94**, 100—111. Compare this vol., ii, 14, 15, 163).—The relation between the atomic number and the characteristic frequency of an element is considered with reference to the theory of probability, and it is shown that the chance of the relation being accidental is very small.

According to Rydberg, there are two unknown elements between hydrogen and lithium, and the atomic number of lithium should be taken as 5 instead of 3, which is the value assigned by Moseley. The relation $Nv=nv_A$ fits the results of observation more closely, however, when Moseley's numbers are used for N. With regard to the physical significance of the relation, it is supposed that the energy of the nucleus is an integral multiple of a certain quantity of energy characteristic of that condition of the atomic system which corresponds with the limiting frequency.

The similar relation connecting the atomic number and the electronic frequency is supposed to indicate that in the limiting conditions which are associated with the maximum of the photoelectric effect, the ionisation potential, and the thermionic potential we are dealing with a minimum value of the energy of the atomic system. H. M. D.

Molecular Frequency and Molecular Number. II. The Frequency of the Longer Residual Rays. H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 404—409. Compare this vol., ii, 14, 163).—According to the results previously communicated, it would seem that the product of atomic number and atomic frequency in the case of an element, or of molecular number and molecular frequency in the case of a compound, is an integral multiple of a fundamental frequency which is approximately equal to 21×10^{12} sec.$^{-1}$ In order to obtain the frequency of vibration of the atoms in compounds, recourse may be had to the residual rays which are obtained by repeated reflections from the surfaces of solids, and have been investigated by Rubens (compare A., 1910, ii, 172; 1913, ii, 648; 1914, ii, 236). By reference to the available data for the wave-lengths of the residual rays for various inorganic compounds, further evidence is obtained in support of the above relation between the molecular number and the molecular frequency.

The results obtained in this and the preceding papers suggest that the forces binding the atoms in the molecule are similar in character to those which bind the molecules of a solid. To account for the integral relations, it must be assumed that there is something of a discrete character in the nature of these forces, and the suggestion is made that the linkings between the atoms are constituted by Faraday tubes of force, which would then be regarded as physical entities.　　　　　　　　　　　　　　H. M. D.

Device for Preventing Back-flow in Water Pumps. MESTREZAT (*Ann. Chim. anal.*, 1918, **23**, 84—85).—An ordinary bicycle valve suitably fitted in the pipe connecting the pump with the vessel from which the air is to be exhausted prevents water passing into the latter.　　　　　　　　　　　　　　W. P. S.

Modification of the Soxhlet Extractor.　J. W. WEIR (*J. Lab. and Clin. Med.*, St. Louis, 1917, **3**, 204; from *Physiol. Abstr.*, 1918, **3**, 4).—A modification for use in the extraction of liquids is described and figured in the original.　　　　　　W. G.

New and Simple Ultra-filters. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 72—76).—Ultra-filters of simple construction for the filtration of colloidal solutions are described. It has been found that an efficient apparatus may be obtained by the use of either an ordinary or a Büchner funnel and filter paper which has been treated in situ with a 2% collodion solution. The best results were obtained, however, by the use of a Schleicher and Schüll Filtrierhut M 577 treated in the same way with the colloidal solution. The results obtained by subjecting a number of colloidal solutions of different kinds to ultra-filtration in this apparatus are described.　　　　　　　　　　　　　　　　　　H. M. D.

Inorganic Chemistry.

Recovery of [Iodine from [Dilute Residues. HERBERT
F. STEPHENSON (*Analyst*, 1918, **43**, 165—166).—The iodine is
precipitated as mercuric iodide by treating the neutral or slightly
acid liquid with mercuric chloride; when a suitable quantity of the
iodide has been collected, it is treated at about 45° with a mixture
of nitric and hydrochloric acids (1:5), then cooled, and the
liberated iodine collected. Four parts of the moist iodine are now
added in small quantities to a mixture of 1 part of iron filings and
10 parts of water; the mixture is boiled subsequently, treated
with a slight excess of potassium hydroxide, the precipitated ferric
hydroxide is separated, and the potassium iodide recovered by
evaporating the solution. [See, further, *J. Soc. Chem. Ind.*, June.]
W. P. S.

A Third Kind of Sulphur Molecule. V. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam,* 1918, **20**, 824—830. Compare A., 1915, ii, 254).—Equilibrium between the two forms of sulphur, S_λ and S_π, is attained less rapidly in toluene than in sulphur chloride. At 140°, six hours are required in the case of toluene, whereas equilibrium is reached in a few minutes in sulphur chloride solution.

Solutions of sulphur in toluene, in which equilibrium between S_λ and S_π had been established by heating at 140°, 150°, and 160°, were cooled to 0° and stirred for an hour in contact with rhombic sulphur; the sulphur content of the resulting solution was then determined, and from the results the proportions of S_λ and S_π in the solutions examined are derived. The proportion of S_π increases with the temperature and also slightly with the concentration. Under similar conditions, the proportion of S_π is considerably smaller in toluene than in sulphur chloride, but is approximately the same when toluene and carbon disulphide are used as solvents. H. M. D.

Selenic Acid and Iron. Reduction of Selenic Acid by Nascent Hydrogen and Hydrogen Sulphide. Preparation of Ferrous Selenate and Double Selenates of the Iron Group. A. E. H. TUTTON (*Proc. Roy. Soc.,* 1918, [A], **94**, 352—361).—In an attempt to prepare ferrous selenate by the action of metallic iron on a solution of selenic acid, it was found that the iron becomes covered with a film of selenium which greatly retards the reaction and renders this method practically useless. No hydrogen is evolved, and the formation of the selenium would appear to be due to the reducing action of nascent hydrogen on the selenic acid, $6H + H_2SeO_4 = Se + 4H_2O$. The net result of such slow action as occurs may therefore be represented by the equation $3Fe + 4H_2SeO_4 = 3FeSeO_4 + Se + 4H_2O$. When the iron is replaced by zinc, hydrogen is given off, and very little reduction of selenic acid occurs. In the case of magnesium, hydrogen is also evolved, but reduction takes place to a considerable extent.

The reaction between ferrous carbonate (in the form of chalybite) and selenic acid also occurs very slowly, and for this reason cannot be used for the preparation of ferrous selenate. Solutions of this substance were readily obtained, however, by the action of ferrous sulphide on a concentrated solution of selenic acid. The hydrogen sulphide liberated in the primary reaction reduces the selenic acid to some extent in accordance with the equation $3H_2S + H_2SeO_4 = Se + 3S + 4H_2O$, but this does not interfere with the application of the method. If the filtered solution is allowed to crystallise, monoclinic crystals of $FeSeO_4,7H_2O$ isomorphous with $FeSO_4,7H_2O$ are obtained. The crystals of the selenate are much less stable than those of ferrous sulphate, and become opaque with such rapidity that it has not been possible to make any accurate goniometric observations with them.

The double selenates of the type $M_2SeO_4,FeSeO_4,6H_2O$ are

readily obtained in the case of rubidium, cæsium, and ammonium. The corresponding potassium double selenate crystallises out if the temperature is not much higher than 0°. At the ordinary temperature, very small, monoclinic crystals of the dihydrated salt separate out.   H. M. D.

Telluric Acid and its Alkali Salts in their Behaviour as Semi-colloids. ARTHUR ROSENHEIM and GERHART JANDER (*Kolloid Zeitsch.*, 1918, **22**, 23—44).—The investigation of telluric acid and its alkali salts has shown that these readily undergo polymerisation, with the formation of substances of semi-colloidal or colloidal character, according to the degree of polymerisation.

Measurements of the hydrogen ion concentration of $1N$-telluric acid solution gave $[H^{\cdot}] = 4 \times 10^{-5}$ gram ion per litre. On the assumption that the acid ionises in accordance with the equation $H_6TeO_6 = H^{\cdot} + H_5TeO_6{}'$, this gives $K = 1 \cdot 6 \times 10^{-4}$ for the ionisation constant. According to this result, telluric acid is a very weak acid, approximating very closely to boric acid and hydrocyanic acid. This is in agreement with the very small value of the molecular conductivity, which increases from $0 \cdot 1902$ for $v = 4$ to $0 \cdot 6913$ for $v = 1024$ litres per gram molecule.

Freezing-point and boiling-point measurements for telluric acid solutions were also made, and these observations are in general agreement with the evidence afforded by the electrical measurements. Irregularities in the boiling points were found which are attributed to the formation of modifications of telluric acid of colloidal character. That the constitution of the aqueous solutions changes with rise of temperature is shown by the abnormally large value of the temperature coefficient of the molecular conductivity. The facts suggest that the more complex modification formed as the temperature rises is more strongly ionised than the modification which is represented by the crystalline acid. The so-called *allo*telluric acid described by Mylius (A., 1901, ii, 550) represents such a polymerised modification of greater conductivity. When aqueous solutions of *allo*telluric acid are kept at 25°, the conductivity falls, and ultimately reaches the value which is characteristic of the crystallised acid. The depolymerisation is also shown in other properties of the solution, but the milky appearance indicates that small quantities of a colloidal, insoluble modification are present. In view of this behaviour, it would seem that *allo*telluric acid is not a homogeneous modification, but consists of a mixture of polymerised forms differing considerably in complexity.

The investigation of the sodium, lithium, and potassium salts has shown that these behave in many ways like the free acid. These salts have no definite solubility in water; the quantity of water which the crystals contain varies according to the concentration of the solutions from which they are deposited, and the crystals undergo dehydration without any appreciable change in appearance. In these and other respects the salts resemble colloids. They not only absorb water, but experiments made with

lithium tellurate show that the basic salts which have been described are in all probability adsorption compounds formed by the adsorption of lithium hydroxide from the solution. In a similar way, experiments made with potassium tellurate indicate that the so-called acid salts are adsorption compounds containing variable proportions of adsorbed telluric acid. In view of these observations, the statements made with respect to the alkali tellurates in the older literature must be accepted with reserve.

In the course of this investigation, solutions containing telluric acid and potassium nitrate was found to deposit large crystals of the composition $2KNO_3,H_6TeO_6,2H_2O$. This substance can be recrystallised from dilute solutions of potassium nitrate without decomposition. With silver nitrate, the acid forms the compound $AgNO_3,H_6TeO_6$.

Reference is made to the fact that telluric acid readily crystallises with other salts, for example, with phosphates, arsenates, iodates, and oxalates. The formation of these additive compounds is supposed to be connected with the weak acid nature of telluric acid. H. M. D.

Recent Studies on Active Nitrogen. (Hon.) ROBERT JOHN STRUTT (T., 1918, **113**, 200—209).—A lecture delivered before the Chemical Society on February 21st, 1918. H. M. D.

Nitride Formation. E. B. MAXTED (*J. Soc. Chem. Ind.*, 1918, **37**, 105—109).—The available data for the influence of temperature on the specific heats of nitrogen, hydrogen, and ammonia lead to the conclusion that the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$ will be displaced with rise of temperature in favour of the elementary gases, but that the proportion of ammonia will reach a minimum at a certain temperature and at higher temperatures will increase as the temperature rises. With the object of testing this result, which depends on an extrapolation of the formulæ connecting the specific heats of the gases with the temperature, the author has investigated the formation of ammonia at high temperatures by rapidly cooling the hot gaseous mixtures.

In one of the methods employed, the mixture of nitrogen and hydrogen was injected into an oxy-hydrogen flame burning under water, the ammonia contained in the water at the end of the experiment being estimated colorimetrically or by direct titration. The proportion of the injected mixture of nitrogen and hydrogen was varied in different experiments, resulting in changes in the flame temperature which could be approximately estimated. From the quantities of ammonia actually found in the several experiments, the author calculates the amount which would have been formed if the gas mixture consisted entirely of nitrogen, hydrogen, and ammonia at atmospheric pressure. In this way, it has been found that the proportion of ammonia increases from 0·0027 vol. % at 1280° (abs.) to 1·23 vol. % at 2580° (abs.).

In other experiments, the flame was cooled by contact with a water-cooled quartz tube. Under these conditions, the cooling is

less rapid, and although these experiments show also that the equilibrium proportion of ammonia increases rapidly with the temperature, the quantities obtained were less than those in which the hot gaseous mixture was directly cooled by water.

The possibility of obtaining iron nitride by direct combination of nitrogen with the finely divided metal has also been examined. Although iron nitride begins to give off nitrogen at about 500° and decomposes rapidly at 600°, experiments in which finely divided iron was subjected to the action of nitrogen at 100 atmospheres between 500° and 700° showed no evidence of the formation of nitride. In view of this negative result, attempts were then made to determine the dissociation pressure of iron nitride. The nitride was slowly raised in temperature to 600°, and then allowed to cool slowly, the pressure being read off at various temperatures. Experiments were made for various initial nitrogen pressures, and although in all cases decomposition of the nitride took place at 600°, there was no evidence of recombination during the cooling process. In other words, equilibrium conditions are not realisable. The results obtained, however, suffice to show that iron nitride cannot be synthesised under the conditions obtaining in these experiments.   H. M. D.

The Production of Nitric Acid from Nitrogen Oxides.

GUY B. TAYLOR, JULIAN H. CAPPS, and A. S. COOLIDGE (*J. Ind. Eng. Chem.*, 1918, **10**, 270—275).—If a mixture of nitric oxide with excess of air from an oxidising plant is cooled and allowed sufficient time to oxidise to nitrogen peroxide, it will react with sulphuric acid in accordance with the equation $2NO_2 + H_2SO_4 = HNO_3 + HNOSO_4$, and on electrolysis of the nitrososulphuric acid, the following reaction may take place: $HNOSO_4 + 2H_2O = HNO_3 + H_2SO_4 + H_2 + 2$ farads. In practice, however, the process is only efficient at first, since nitric acid or nitrososulphuric acid diffuses through the diaphragm and is reduced to nitric oxide with some free nitrogen. The chemical reactions involved in the conversion of nitric oxide to nitric acid in the arc and ammonia oxidation processes are:

(1) $2NO + O_2 \rightleftarrows 2NO_2$.
(2) $2NO_2 + H_2O \rightleftarrows HNO_3 + HNO_2$.
(3) $3HNO_2 \rightleftarrows HNO_3 + 2NO + H_2O$.

Of these reactions, the first is the controlling one, and for this reason as much space as practicable should be allowed for the reaction in the plant. This reaction begins to proceed from left to right as soon as the gases have cooled below 600°, but is not complete even in the presence of a large excess of oxygen until the temperature reaches 200°. Since the reaction has a negative temperature coefficient, it is necessary to cool the gases as much as possible before entering the absorption system. [See also *J. Soc. Chem. Ind.*, June.]   C. A. M.

Amount of Phosphoric Acid in the Sea-water off Plymouth Sound. DONALD J. MATTHEWS (*Reprint : J. Marine Biol. Assoc. United Kingdom*, 1917, **11**, 251—257. Compare A., 1916, ii, 635).—The amount of phosphoric acid in sea-water off Plymouth reached a maximum (0·06 mg. of P_2O_5 per litre) in December, 1915; it then decreased irregularly to a minimum (less than 0·01 mg. per litre) in April—May, 1916, and again attained the same maximum as before in January, 1917. This seasonal variation is probably due to the removal of phosphates from solution by algæ, diatoms, etc.   W. P. S.

The Fundamental Polyhedron of the Diamond Lattice. ELLIOT Q. ADAMS (*J. Washington Acad. Sci.*, 1918, **8**, 240).—The author has found that the convex polyhedron with a symmetry corresponding with the point-system of the diamond space-lattice is the dodecatetrahedron $k(111),(110)$. The arrangement of this in space constitutes a kind of twinning, which explains the fact that diamond is crystallographically holohedral, but the unit polyhedra are hemihedral.   A. B. S.

Oxidisable Constituents of Coal. I. J. I. GRAHAM and J. HILL (*Trans. N. Eng. Inst. Min. Eng.*, 1918, **68**, 37—54).—Coal from the Barnsley soft seam was extracted with pyridine at 40° and 60 mm. pressure in an atmosphere of nitrogen. This was intended to prevent or minimise the absorption of oxygen and pyridine by the coal, which probably occurred in previous experiments on the extraction of coal with solvents. Ten to fifteen % of extract was obtained. The capacity for absorbing oxygen was determined for the extract, the residue, and ·the original coal by Winmill's method at 30° and 90°, both in air and an atmosphere of 90% oxygen. The absorption by the extract was negligibly small, whilst the avidity of the residue for oxygen was almost equal to that of the original coal. The humic and not the resinic constituent of this coal is the one responsible for tendency to spontaneous combustion. The extract, unlike those described by Wheeler (T., 1913, **103**, 1713), was inert towards a photographic plate, whilst the residue showed a great activity, not, however, due to the oxidation. [See, further, *J. Soc. Chem. Ind.*, 262A.]
                          H. J. H.

Carbonation. II. Carbonation of Distilled Water. H. E. PATTEN and G. H. MAINS (*J. Ind. Eng. Chem.*, 1918, **10**, 279—288).—The rate of evolution of carbon dioxide from distilled water impregnated with carbon dioxide under pressure at 0° was measured by opening the bottle momentarily and noting the time required until the initial pressure was again shown on the pressure gauge. In this way, a series of simultaneous measurements of pressures and times was obtained, and from these data "pressure recovery" curves were constructed, in which the time in minutes represented the abscissæ and the pressure in lb. per square inch

in excess of atmospheric pressure formed the ordinates. With the exception of the first curve corresponding with the first opening, in which an excessive quantity of gas was withdrawn, the curves showed a striking regularity, and were, in general, of a logarithmic type. The anticipated sudden rise of curve and sharp decrease of pressure were not observed. The results indicated that at a high pressure of carbon dioxide there is a close agreement with Henry's law. [See also *J. Soc. Chem. Ind.*, June.]   C. A. M.

Theoretical and Experimental Investigations on Metallic Alloys. N. PARRAVANO (*Ann. Chim. Applicata*, 1918, **9**, 1—86). —The author brings together the results of investigations on binary, ternary, and quaternary alloys made by himself and his collaborators and by De Cesaris, and already published in a series of thirty-seven papers during the years 1910—1917.

T. H. P.

The Stability of Dakin's Sodium Hypochlorite Solution. FRITZ WISCHO and FRANZ FREIBERGER (*Münch. med. Woch.*, 1917, **64**, 1528—1529; from *Chem. Zentr.*, 1918, i, 228).—Concentrated Dakin solutions deteriorate to the extent of about 40% of the sodium hypochlorite in a month; they are comparatively stable when the amount of hypochlorite is reduced to 12·5%, but dilute solutions will keep better still, the decomposition being only about 10% in two months.   J. C. W.

The Double Sulphate of Sodium and Ammonium. C. MATIGNON and F. MEYER (*Compt. rend.*, 1918, **166**, 686—688). —The heat of solution of the double sulphate,

$$Na_2SO_4,(NH_4)_2SO_4,4H_2O,$$
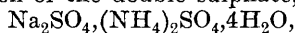
at about 15° is −13·00 Cal., from which the following heats of formation of the double salt may be deduced:

$(NH_4)_2SO_4$ sol. $+ Na_2SO_4$ sol. $+ 4H_2O$ liq. $=$
$\qquad Na_2SO_4,(NH_4)_2SO_4,4H_2O$ sol. $+ 11·04$ Cal.

$(NH_4)_2SO_4$ sol. $+ Na_2SO_4$ sol. $+ 4H_2O$ liq. $=$
$\qquad Na_2SO_4,(NH_4)_2SO_4,4H_2O$ sol. $+ 5·54$ Cal.

$(NH_4)_2SO_4$ sol. $+ Na_2SO_4,10H_2O$ sol. $=$
$\qquad Na_2SO_4,(NH_4)_2SO_4,4H_2O$ sol. $+ 6H_2O$ liq. $- 7·6$ Cal.
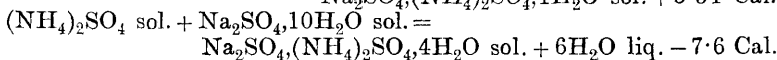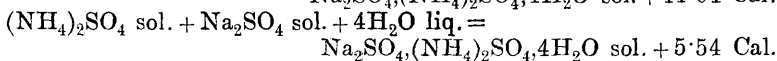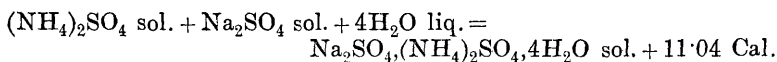
The double salt is stable in the presence of its saturated solution between the temperature limits of 20° and 42°, and thus the salt may be prepared by evaporating a solution containing equimolecular proportions of the two generating salts between these temperatures.   W. G.

Crystals of Barium Disilicate in Optical Glass. N. L. BOWEN (*J. Washington Acad. Sci.*, 1918, **8**, 265—268).—Colourless, six-sided crystal plates with opaque white rims, which form in optical glass rich in barium have been identified with crystals of $BaSi_2O_5$ prepared synthetically. The white outlines are due to minute

crystals which lie along the edges of the larger ones. A small amount of alkali disilicate appears to be contained in solid solution in the crystals in the glass. The plates are orthorhombic crystals with terminal angles 100°, lateral angles 130°, good cleavage parallel to elongation, negative elongation and optical character with $2V = 70°$, refractive indices, $\gamma = 1.617$, $\alpha = 1.598$ in synthetic crystals, slightly lower in crystals in glass, isomorphous with $K_2Si_2O_5$.   A. B. S.

The Ternary System, $MgO-Al_2O_3-SiO_2$. G. A. RANKIN and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], **45**, 301—325).— The ternary system, magnesia–alumina–silica, has been investigated thermally to determine the melting temperatures of the various phases and microscopically to identify the various crystalline substances produced. The various boundary curves of the phases have been determined and the quintuple points fixed. It is shown that the following crystalline substances are stable in contact with the liquid phase: periclase (MgO), corundum (Al_2O_3), tridymite (SiO_2), forsterite ($2MgO,SiO_2$), clinoenstatite (MgO,SiO_2), spinel (MgO,Al_2O_3), sillimanite (Al_2O_3,SiO_2), and a ternary silicate, $2MgO,2Al_2O_3,5SiO_2$, which may be regarded as an end member in the cordierite series. The last compound is unstable at its melting point, and is considerably affected by solid solution. It has been observed in two forms; the μ-form (unstable) crystallises from glass at temperatures below 950°, and is transformed at a somewhat higher temperature into the stable (α) form. The properties of both forms, but more especially those of the α-form, are very like those of the mineral cordierite. Seven quintuple points have been established, two of which are eutectics. The first lies at 1345°±5°, and is for MgO,SiO_2, SiO_2 and the ternary compound; the second lies at 1425°±5°, and is for $SiO_2-Al_2O_3,SiO_2$ and the ternary compound. The third point lies at 1460°±5°, and is for $Al_2O_3,SiO_2-MgO,Al_2O_3$ and the ternary compound; the fourth point lies at 1370°±5°, and is for spinel—$2MgO,SiO_2$ and the ternary compound. Point five lies at 1360°±5°, and is for $2MgO,SiO_2-MgO,SiO_2$ and the ternary compound. The sixth quintuple point is the eutectic point for $2MgO,SiO_2-MgO$ and spinel. It has a melting point 1700°±25°. The last point lies at 1575°±5°, and is for Al_2O_3, spinel, and Al_2O_3,SiO_2. The whole of the experiments were carried out either in a platinum resistance furnace for temperatures below 1600° or in an iridium furnace for higher temperatures. Diagrams and solid models of the system are given to illustrate the equilibria.   J. F. S.

Influence of Cadmium on the Properties of Alloys of Copper and Zinc. LÉON GUILLET (*Compt. rend.*, 1918, **166,** 735—737).—A study of the effect of introducing from 0—4% of cadmium into brasses containing 60% or 70% copper on the mechanical properties of the alloy. Values are tabulated for the

traction, shock, and hardness constants of the alloys, and notes on their micro-structure are given. [See, further, *J. Soc. Chem. Ind.*, June.]   W. G.

Colloidal Arsenates. G. KLEMP and J. VON GYULAY (*Kolloid Zeitsch.*, 1918, **22**, 57—68.   Compare A., 1915, ii, 256).—If solutions of potassium dihydrogen arsenate and zinc sulphate of appropriate concentration are brought together, there is no precipitation, but a jelly containing zinc hydrogen arsenate is formed. The same result is obtained if the zinc sulphate solution is mixed with solutions of disodium hydrogen arsenate or trisodium arsenate which have been previously neutralised by the addition of hydrochloric or acetic acid.   When the jellies are kept for two or three months, crystals begin to separate.   The crystals which separate from the jellies prepared from trisodium arsenate neutralised by acetic acid have the composition
$$Zn_3(AsO_4)_2,2ZnHAsO_4,4H_2O,$$
whilst those separating from the jellies prepared from potassium dihydrogen arsenate or from trisodium arsenate neutralised by hydrochloric acid consist of zinc hydrogen arsenate, $ZnHAsO_4,H_2O$.   H. M. D.
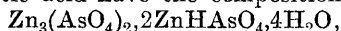
Sub-bromide and Sub-chloride of Lead. HENRY GEORGE DENHAM (T., 1918, **113**, 249—256).—The method previously described for the preparation of lead sub-iodide (T., 1917, **111**, 29) has been extended to the corresponding bromine and chlorine compounds, the sub-bromide being obtained by the action of ethyl bromide vapour on lead sub-oxide at 261°, and the sub-chloride by the action of ethyl chloride on the sub-oxide at 311°.   The two sub-compounds are grey in colour, fairly stable in the air, but are readily oxidised by bromine water or by permanganate solution. They are readily decomposed by acids with the formation of the normal salts and the metal.

The sub-salts are sparingly soluble in water.   On the assumption that the salts are completely ionised and that the ions have the same mobility as those of the normal salts, the electrical conductivities of the saturated solutions give 2·2 milli-equivalents per litre for the solubility of the sub-chloride and 0·4 milli-equivalent for that of the sub-bromide.   H. M. D.

The Rare Earths.   V.   Holmium and Dysprosium. H. C. KREMERS and C. W. BALKE (*J. Amer. Chem. Soc.*, 1918, **40**, 593—598.   Compare A., 1917, ii, 259, and following abstract).— The concentration of dysprosium and holmium in a mixture of the yttrium earths, and the separation of holmium from yttrium have been studied.   It is found that the fractionation of the bromates of the yttrium earths effects a rapid and efficient concentration of dysprosium and holmium.   Starting with 12 kilos. of rare earth oxalates from gadolinite, which were converted into bromates, three parallel series of fifty recrystallisations were carried out.   The series showed a concentration of

samarium, neodymium, and praseodymium toward the insoluble end, dysprosium and holmium in the central portion, and yttrium, thulium, and erbium toward the soluble end. At this point, the material rich in dysprosium and holmium was removed from the three series, combined, and made into three new series, A, B, and C. Series A consisted of the more soluble fractions, and contained dysprosium, holmium, erbium, and yttrium. Series B contained the fractions richest in holmium and dysprosium, with small amounts of neodymium, praseodymium, erbium, and yttrium. Series C was composed of the less soluble bromates, and contained holmium, dysprosium, terbium, neodymium, praseodymium, and traces of erbium and yttrium. The three series were fractionated in parallel. The concentration of the earths in the different series was controlled mainly by the colour of the solutions. As the holmium and dysprosium became concentrated toward the less soluble end of series A, these fractions were added to series B, placing them where the fractions showed a similar colour. From series C, the more soluble dysprosium and holmium were removed and added to series B in the same way. In the same manner, yttrium and erbium which collected in the soluble end of series B were added to series A, and the neodymium and praseodymium from the less soluble end of B were placed in C. The three series were recrystallised thirty times, which caused most of the dysprosium and holmium to collect in series B; was eventually given a further sixty recrystallisations, which caused the holmium and dysprosium to concentrate very rapidly. A difficulty was experienced due to the repeated separation of cerium basic bromate as a brown sludge. It is therefore recommended that the cerium be removed by the sodium sulphate method before the fractionation commences. The separation of holmium from yttrium was also studied (i) by fractional precipitation with lactic acid, (ii) by fractional precipitation with ammonium carbonate, and (iii) by fusion of the nitrates. The first two methods were entirely unsuccessful. The fusion of a mixture of samarium, yttrium, and holmium nitrates gave a rapid concentration of the holmium. A mixture which had an equivalent of 98·6 at the start gave after thirty-one fusions four end fractions with equivalents 154·2—155·3. Attempts to separate holmium and yttrium by this method failed, and it was only after the addition of samarium that the separation became possible.   J. F. S.

The Rare Earths. VI. Purification and Atomic Weight of Dysprosium. H. C. KREMERS, B. S. HOPKINS, and E. W. ENGLE (*J. Amer. Chem. Soc.*, 1918, **40**, 598—611. Compare A., 1917, ii, 259, and preceding abstract).—A short history of the knowledge of the element dysprosium is given in the paper. A quantity of dysprosium material of a high state of purity was further fractionated as ethyl sulphates and as bromates. It is shown that the ethyl sulphates are more efficient for the separation of dysprosium from neodymium, praseo-

dymium, and terbium, and that neither of the methods is efficient for the separation of holmium from dysprosium. The atomic weight of dysprosium has been determined from the ratios (i) dysprosium sulphate to dysprosium oxide, (ii) dysprosium oxide to dysprosium chloride, and (iii) dysprosium chloride to silver. It is shown that the octahydrate of dysprosium sulphate is not constant in composition when dried over sulphuric acid, consequently the ratio $Dy_2(SO_4)_2,8H_2O : Dy_2O_3$ does not give trustworthy values for the atomic weight. The value $Dy = 163.83$ was obtained as the mean of nine experiments from the ratio $DyCl_3 : Dy_2O_3$, but since, on further investigation, it was shown that the oxide prepared for these experiments from the oxalate was not constant in composition, this value is rejected. By no method tried could an oxide be obtained which yielded concordant results from this ratio. Eight experiments were made to determine the ratio $DyCl_3 : 3Ag$, and the value 162.52 obtained. This is put forward as the most likely value, and is considerably lower than the result obtained (164.228) previously (*loc. cit.*).   J. F. S.

Determination of the Velocities of Cooling necessary to realise the Tempering of Carbon Steels. P. CHEVENARD (*Compt. rend.*, 1918, **166**, 682—685).—A continuation of previous work (compare A., 1917, ii, 414). Using the method previously described (*loc. cit.*), and working with steels containing from 0·2—0·8% carbon, the author has determined, for different temperatures of heating, in the diagram plotting carbon content against velocity of cooling, the curves which mark the limit of appearance of martensite. The results indicate that, from the point of view of the effectiveness of tempering, an insufficient velocity of cooling can, to a certain extent, be compensated by an elevation of the temperature of heating. This compensation is less adequate as the carbon content of the steel diminishes. [See, further, *J. Soc. Chem. Ind.*, June.]   W. G.

The Reduction of Osmium Tetroxide by Hydrogen Chloride. JAROSLAV MILBAUER (*J. pr. Chem.*, 1917, [ii], **96**, 187—189).—During experiments the results of which indicated that the chlorides of most metals are without appreciable influence on the rate of oxidation of aqueous hydrogen chloride by free oxygen or air, it has been found that, contrary to the general belief (compare Dammer, "Handbuch," III, p. 919), osmium tetroxide is reduced by concentrated hydrochloric acid with production of chlorine, the chemical change being representable by the equation $2OsO_4 + 12HCl = 2OsO + 6Cl_2 + 6H_2O$.   D. F. T.

Mineralogical Chemistry.

The Auriferous Minerals of the Côte d'Ivoire. F. ROUX (*Compt. rend.*, 1918, **166**, 645—646).—A sample of the metallic portion of a quartz, without visible gold, from Kokumbo gave on analysis: Au = 8·63%, Bi = 48·36%, Cu = 1·82%, Te = 37·52%, Ag = trace, S = 3·65%. Two metallic samples from the mineral at Poressou were each found to contain tellurium and bismuth.

W. G.

Analytical Chemistry.

Accurate Method for taking "Aliquots" in Volumetric Analysis. HERBERT E. EASTLACK (*J. Amer. Chem. Soc.*, 1918, **40**, 620—622).—The author describes a method of taking aliquot parts of solutions for analysis, based on that of Miller (this vol., ii, 80), which is claimed to be simpler, more rapid, and more accurate than Miller's method. The newer method differs from the earlier one mainly in titrating the residue after the titrations have been made, instead of evaporating to dryness and weighing it.

J. F. S.

Detection and Estimation of Bromine by Magenta-Sulphuric Acid Reagent. G. DENIGÈS and L. CHELLE (*Ann. Chim. anal.*, 1918, **23**, 81—83).—The influence of nitrous acid on the detection of bromine by the magenta–sulphuric acid method described previously (A., 1913, ii, 72) may be prevented by carrying out the test at a temperature not exceeding 16°. Five c.c. of the bromide solution (containing not more than 1 gram of bromine per litre) are treated with 4 drops of concentrated hydrochloric acid, 4 drops of 10% potassium chromate solution, and 1 c.c. of concentrated sulphuric acid; the mixture is cooled at once to 15°, and 1 c.c. of the magenta reagent and 1 c.c. of chloroform are added; the chloroform is coloured red when the mixture is shaken, the intensity of the coloration depending on the quantity of bromine present.

W. P. S.

New General Method for Determining Iodine in Inorganic and Organic Compounds. N. TARUGI (*Gazzetta*, 1918, **48**, i, 1—16).—This method is based on the reaction $6FeSO_4 + 3H_2SO_4 + 2ICl_3 = 3Fe_2(SO_4)_3 + I_2 + 6HCl$. The iodine formed is extracted by means of chloroform and titrated with thiosulphate, whilst the chlorine is determined by titrating with permanganate

the residual acid solution from the extraction, this containing the ferric sulphate and the excess of the ferrous sulphate. In this way, the proportions of iodine and chlorine, and thus those of iodine trichloride and monochloride in a solution of iodine trichloride, are obtained.

By simple methods, the iodine in an inorganic or organic compound may be converted into iodine trichloride and then estimated as above. [See, further, *J. Soc. Chem. Ind.*, 285A.]   T. H. P.

Oxidation of Sulphides with Potassium Iodate. REGINALD S. DEAN (*J. Amer. Chem. Soc.*, 1918, **40**, 619—620).— In a previous paper (A., 1915, ii, 480), it was shown that in the estimation of sulphides by oxidation with potassium iodate in the presence of hydrochloric acid, the amount of sulphur oxidised to sulphuric acid depended on the concentration of the acid, and that with an amount of iodate equivalent to the sulphide, the maximum amount of oxidation is represented by the equation $3MS + 3KIO_3 + 12HCl \rightleftharpoons 3MCl_2 + 2S + H_2SO_4 + 3KCl + 3ICl + 5H_2O$. It is now shown that with an excess of iodate and hydrochloric acid of any strength sufficient to prevent the hydrolysis of the iodine chloride formed, the whole of the sulphur is quantitatively oxidised to sulphuric acid according to the equation $H_2S + 2KIO_3 + 4HCl \rightleftharpoons 2ICl + H_2SO_4 + 2H_2O + 2KCl$. The estimation is carried out as follows. A solution of hydrogen sulphide is treated with the requisite excess of potassium iodate solution and hydrochloric acid (6—$3N$), and the excess of iodate estimated by means of a standard iodine solution. The method has also been applied to the estimation of lead sulphide; the freshly precipitated lead sulphide is introduced into the iodate solution, hydrochloric acid added, and the titration completed as before. The results in both cases agree within $0 \cdot 1\%$ of the theoretical value.   J. F. S.

The Estimation of Thio-esters in Urine. LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 360—363).—The author considers that Gauvin's method (A., 1914, ii, 142) of hydrolysis of the thio-esters by boiling the urine with one-fifth its volume of hydrochloric acid for fifteen minutes gives satisfactory results in the estimation of these constituents in urine.   W. G.

Two Methods of Destruction of Organic Substances in Urine. LUCIEN CORDIER (*J. Pharm. Chim.*, 1917, [vii], **16**, 363—367).—In the first method, 20 c.c. of urine are evaporated to dryness with 4 grams of a mixture of equal parts of potassium nitrate, anhydrous potassium carbonate, and anhydrous sodium carbonate. The dry residue is intimately mixed with a further 8 grams of the fusion mixture and fused until all the carbon is oxidised. The second method is a modification of that of Gautier and Clausmann for animal tissues (compare A., 1917, ii, 421). Twenty c.c. of urine are evaporated to dryness with 2 grams of magnesium nitrate, and the dry residue is strongly heated until

all the carbon is burnt off. The residue from either fusion may
be used for the estimation of total sulphur in urine.   W. G.

**Detection of Carbon Dioxide in the Analysis of
Carbonates or Oxalates.** O. F. STAFFORD (*J. Amer. Chem.
Soc.*, 1918, **40**, 622).—In order to detect the presence of carbon
dioxide in the gaseous products of the action of acids on minerals,
the author inserts a glass tube into the mouth of the test-tube;
this tube is drawn out to a capillary fine enough to cause a drop
of the reagent (baryta water) to remain in it, and not too fine to
prevent bubbles of the gas being drawn upward through the liquid.
To make the test, the gas from the test-tube is drawn through the
baryta water by aspirating at the top of the inserted tube. The
method may be made roughly quantitative for small traces of
carbonates or oxalates. Two such capillaries are used; the material
to be examined is placed in one, and the second tube, containing
a drop of baryta water, inserted into the mouth of the first and
sealed to it by means of " Khotinsky " cement. Then by aspirating
a drop of 30% sulphuric acid is drawn on to the material, and the
gas generated drawn through the baryta water. In the case of
oxalates, 30% sulphuric acid mixed with potassium permanganate
is used. The turbidity produced in the baryta water is compared
with turbidities produced similarly from known amounts of
carbonates or oxalates.   J. F. S.

Water Analysis in the Field. GEORGE W. HEISE and A. S.
BEHRMAN (*Philippine J. Sci.*, 1918, **13**, [A], 1—17).—The methods
are based on those of Leighton [U.S. Geol. Survey, Water Supply
Paper (1905) No. 151], and bacteriological examination is also
made. Titrations are effected with reagents in pellet form. [See,
further, *J. Soc. Chem. Ind.*, June.]   H. J. H.

Detection of Potassium by the Use of Light Filters.
ALOIS HERZOG (*Chem. Zeit.*, 1918, **42**, 145).—The light filter
recommended is prepared by coating a glass plate with a gelatin
solution containing a mixture of the two dyes patent blue and
tartrazin in such proportion that each sq. metre of glass shall
have on it 3·9 grams of the former and 2·5 grams of the latter
dye. Viewed through this screen, the potassium flame appears
bright red surrounded by a yellowish-green fringe. Rubidium is
the only other element which gives a coloration similar to that
shown by potassium. Green and violet dyes may be used for the
purpose, but preference is given to the mixture mentioned.
                                                    W. P. S.

**Iodide Titration of Silver Nitrate with Palladous
Nitrate as Indicator.** LOUIS SCHNEIDER (*J. Amer. Chem. Soc.*,
1918, **40**, 583—593).—The Volhard method for the volumetric
estimation of silver is interfered with by the presence of certain
metals and loses its sensitiveness for very dilute solutions. The

author describes a method whereby silver solutions may be titrated
with iodide in the presence of such metals and in very dilute solu-
tion by use of a solution of palladous nitrate as indicator. The
indicator is prepared by dissolving 0·06% of palladous nitrate in
16% nitric acid; it is found advisable to use a protective colloid
along with the indicator to prevent the occlusion of potassium
iodide or silver nitrate. For this purpose, a 5% solution of gum
arabic is found most advantageous. The indicator is converted
by the first excess of iodide into palladous iodide, which gives a
red colour to the solution; this action is sensitive to 1 part in
500,000. This method is further to be recommended on account
of the accuracy and easy reproducibility with both $N/10$- and
$N/1000$-solutions. The author discusses at some length the
possible errors of the method, and gives full details of the pro-
cedure to be adopted for $N/10$- and $N/1000$-solutions.   J. F. S.

**Field Methods for the Determination of the Total
Hardness of Water.** A. S. BEHRMAN (*Philippine J. Sci.*, 1918,
13, [A], 21—27).—Blacher's method of titration with potassium
palmitate has been adapted to field conditions. The water is
titrated with standard pellets of the reagent. [See, further, *J.
Soc. Chem. Ind.*, June.]   H. J. H.

Analysis of Glass. L. RONNET (*Ann. Falsif.*, 1918, **11**,
26—31).—A scheme is given for the analysis of glass containing
silica, iron, aluminium, manganese, calcium, magnesium, potassium,
and sodium. The usual methods of separating and estimating these
constituents are employed. [See, further, *J. Soc. Chem. Ind.*,
1918, 266A.]   W. P. S.

**Estimation of the Reducing Power of Urine, both free
from and containing Dextrose, by means of an Alkaline
Glycerol–Copper Solution.** H. RUOSS (*Zeitsch. physiol. Chem.*,
1918, **101**, 131—164).—The method previously described (A., 1917,
ii, 549) is modified by employing a glycerol–copper solution and by
using always the same volume of urine with varying quantities of
copper solution instead of maintaining a constant volume of the
latter and varying the former. The glycerol–copper solution is
prepared by dissolving 3·464 grams of copper sulphate in 10 c.c.
of hot water, cooling, and adding 15 c.c. of glycerol and 22 c.c.
of sodium hydroxide solution (D 1·357). The mixture is again
cooled, 5 c.c. of a 30% potassium thiocyanate solution added, and
then the volume brought to 100 c.c. by the addition of 25% sodium
chloride solution. For an estimation, 5 c.c. of urine are treated
with from 0·1 to 1 c.c. of the new reagent, and, after boiling, the
end-point determined in the manner previously described (*loc. cit.*).
The amount of copper solution is varied until it is exactly reduced
by the dextrose or other reducing substances present in the urine.
    Attention is directed to the fact that the reducing power of
urine free from sugar is proportional to $D-1$, where D is the

specific gravity of the urine, and that the urine may be freed from substances containing nitrogen by treatment with an excess of the Patein-Schöndorff mercuric nitrate reagent (A., 1908, ii, 311), the excess of mercury being subsequently removed by precipitation with alkali followed by zinc dust.   H. W. B.

Copper–Phosphate Mixtures as Sugar Reagents. A Qualitative Test and a Quantitative Titration Method for Dextrose in Urine. OTTO FOLIN and W. S. McELLROY (*J. Biol. Chem.*, 1918, **33**, 513—519).—The qualitative reagent is prepared by dissolving 100 grams of sodium pyrophosphate (U.S.P.), 30 grams of crystallised disodium hydrogen phosphate, and 50 grams of anhydrous sodium carbonate in about a litre of water, and adding 13 grams of copper sulphate previously dissolved in about 200 c.c. of water. The solution appears to keep indefinitely and is cheaply prepared. To test for reducing sugars, 5 c.c. of the reagent are placed in a test-tube, five to eight drops (not more than 0·5 c.c.) of the urine added, and the mixture boiled for one minute, or heated in boiling water for three to five minutes. Minute traces of sugar are indicated by various grades of turbidity, larger amounts by unmistakable precipitates of cuprous oxide. A slight turbidity occurring after cooling may be due only to the reducing action of normal urine.

For quantitative estimation, the only solution required is an acidified copper sulphate solution containing 60 grams of crystallised copper sulphate and 4 c.c. of concentrated sulphuric acid per litre. Five c.c. of this solution correspond with 25 mg. of dextrose or lævulose, 45 mg. of anhydrous maltose, or 40·4 mg. of anhydrous lactose. The other necessary reagent is a dry mixture containing 100 grams of crystallised disodium hydrogen phosphate, 60 grams of dry sodium carbonate, and 30 grams of sodium or potassium thiocyanate. The authors recommend the titrations to be made in test-tubes, using undiluted urine. This simplification is made possible by attaching to the tip of an ordinary 25 c.c. glass-stoppered burette another tip consisting of a glass tube drawn out at one end to an almost capillary bore, and delivering between forty-five and fifty-five drops of urine per c.c. If the burettes carrying accessory tips are filled by suction, the necessity of rinsing the burette with the sugar solution to be titrated is avoided, which can be proved by filling the burette with water after it has just been emptied from a urine containing 5% of sugar. On testing the water in the lower part of the burette, it is found to be quite free from sugar. To carry out an estimation, 5 c.c. of the copper reagent and 4 to 5 grams of the dry salt mixture are heated in a test-tube until a·clear solution is obtained (a pebble is added to prevent bumping). Twenty-five drops of urine are run in from the burette, and the mixture gently boiled for two minutes. If the solution is still blue, more urine is run in, boiling for one minute after each addition, until the solution is colourless. From the total number of drops, the volume of urine added can be computed,

and hence the percentage of dextrose in the urine. The results of the titration should be confirmed by a repetition, in which the first addition of urine should be only two or three drops less than the full amount of urine required. The total period of boiling must not be less than four or more than seven minutes.

The presence of albumin in the urine does not obscure the end-point of the titration. The use of the test-tube instead of a flask or beaker greatly retards the reoxidation of the cuprous oxide and materially aids the rapid performance of the test. If desired, a 5 c.c. burette graduated in 0·02 c.c. divisions may be used instead of the ordinary burette with capillary tip described above.

<div align="right">H. W. B.</div>

Estimation of Lactose in Milk. OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1918, **33**, 521—524).—The authors describe two methods, based on titration and colorimetry respectively, the former being considered to give the more nearly accurate results. In the titration method, the reagents and apparatus described for the estimation of dextrose in urine (preceding abstract) are employed, and neither the protein nor the fat is previously removed from the milk. The milk is simply diluted with water (1:4) and added directly to the copper–phosphate solution, boiling being continued rather longer than in the estimation of dextrose.

For the colorimetric estimation, a modification of Dehn and Hartman's method (A., 1914, ii, 223) is described which is based on the colour developed when an alkaline solution of lactose in saturated picric acid is heated for a fixed time at 100°. [See, further, *J. Soc. Chem. Ind.*, 278A.]

<div align="right">H. W. B.</div>

Estimation of Dicyanodiamide in Old Calcium Cyanamide. H. KAPPEN (*Zeitsch. angew. Chem.*, 1918, **31**, 31—32).— A sample of very old calcium cyanamide was found to be free from cyanamide nitrogen; the dicyanodiamide nitrogen was estimated by Caro's and by Hager's methods. The results obtained by these two methods did not agree (compare Hager and Kern, A., 1916, ii, 687), and the author suggests that the difference may be due, in part, to the presence of urea in the sample. This is confirmed by the results of analyses of mixtures of urea and dicyanodiamide; urea has less effect on the results obtained by Caro's method than it has on those found by Hager's method.

<div align="right">W. P. S.</div>

The Spectroscopic-quantitative Estimation of Urochromogen. TRAUGOTT BAUMGÄRTEL (*Biochem. Zeitsch.*, 1918, **85**, 162—170).—The author gives a modification of the method of Weiss for the estimation of urochromogen by oxidation with potassium permanganate, in which the colorimetric method adopted by Weiss is replaced by the detection of excess of permanganate spectroscopically. The method has been applied to the determination of the urochromogen output in the urine in certain pathological cases.

<div align="right">S. B. S.</div>

General and Physical Chemistry.

Double Refraction and Optical Activity of Liquid–Crystalline Substances. FELIX STUMPF (*Jahr. Radioakt. Elektronik*, 1918, **15**, 1—64).—A useful and detailed résumé, including bibliography, of the work since the earlier résumé in the same journal by R. Schenck in 1909, is given in six chapters, entitled : (1) Double refraction of inactive and active substances. (2) Rotation of plane of polarisation. (3) Theory of uniaxial active absorbing crystals. (4) Observations on the state of polarisation oblique to the axis of the advancing waves. (5) The theory of M. Born and its experimental examination. (6) The action of the magnetic field on liquid–crystalline substances.   F. S.

Anomalous Molecular Distribution in Mixed Crystals as the Cause of their Anomalous Double Refraction. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 226—235 ; from *Chem. Zentr.*, 1918, i, 567).—A consideration as to the cause of the internal strains to which the anomalous optical properties of some mixed crystals have been attributed. It is not very probable that during rapid crystallisation correct distribution of the components can occur completely so that the blending is entirely consistent with the symmetry of the space lattice. The disturbance in the molecular distribution will cause a reduction in the linear velocity of crystallisation and a deviation in the properties of the mixed crystal from those expected from its symmetry; both these effects are frequently observed. If an anomalous mixed crystal represents an unstable system, the solubility should be least for the normal mixed crystal, as has, indeed, been observed. It is calculated that the alteration in solubility to be expected from the effect of the internal strains in a certain case is 0·3%, whereas the observed difference in solubility may attain 50%. According to this result, the abnormal arrangement in the crystal lattice exerts a direct influence, and not merely an indirect effect on account of the internal strains.   D. F. T.

Electrical Double Refraction in Liquids. C. BERGHOLM (*Ann. Physik*, 1917, [iv], **54**, 511—518).—The author discusses the question of the dependence of the electrical double refraction on the composition and constitution of organic compounds, and points out that Kerr's constant cannot be considered to offer a suitable basis for the comparison of different substances. In place of Kerr's constant B, the quantity $B_R = B \lambda n M / (K + 2)^2 (n^2 + 2)^2 d$ is proposed, λ being the wave-length of the light used, n the ordinary refractive index, M the molecular weight of the substance, K the dielectric constant, and d its density. The quantity $54 B_R$ represents the " electrical double refraction of the molecular refraction "

for a layer of liquid 1 cm. in thickness and an electrostatic field of unit intensity. The values of B_R for a number of substances are compared, and from this it would seem that in the case of aromatic compounds which have similar absorption spectra, the value of B_R varies but little with the nature of the substituent element or group and its position in the benzene ring.

H. M. D.

The Light Emission of Gases and Mixtures of Gases by Electric Discharges. L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1043—1048).—A summary is given of experiments in which the effect of pressure and of the intensity of the electric discharge on the emission spectra of certain gases and gas mixtures was examined.

The observations made with nitrogen, hydrogen, neon, and helium show that the intensity of the lines and bands is proportional to the energy of the discharge, and that the maximum emission is displaced towards the ultra-violet when the pressure is decreased. Argon behaves quite differently, and the nature of the divergence depends on whether the red or the blue spectrum is emitted. If the intensity is plotted against the strength of the current, curves are obtained which are concave or convex to the current axis, according to whether the red or the blue spectrum is considered.

Observations made on mixtures of non-reactive gases show that there is generally a shift of the maximum towards the ultra-violet which may be interpreted in terms of the pressure effect referred to above. In the case of mixtures of gases which react with each other, the observations show that new bands make their appearance in the discharge spectrum. H. M. D.

Absorption of Ultra-violet Rays by Phenyl Derivatives of Methane. G. MASSOL and A. FAUCON (*Compt. rend.*, 1918, **166**, 819—821).—A study of the absorption spectra of benzene, toluene, and di- and tri-phenylmethanes. The results indicate that benzene and the three phenyl derivatives of methane show a general transparency for the radiations extending from the visible spectrum to $\lambda = 270$ and a selective absorption for the radiations from $\lambda = 270$ to $\lambda = 230$. This selective absorption varies with the different compounds, and the characteristic spectrum of benzene with its narrow bands and its undulating aspect is not found in the phenyl derivatives of methane. Their bands are less numerous, often slightly displaced, and do not all appear at the same time. The transparency diminishes as the molecular weight increases. W. G.

Confirmation of van't Hoff's Hypothesis. Optical Superposition in the Meta-saccharins and Related Substances. EDWIN A. HILL (*J. Amer. Chem. Soc.*, 1918, **40**, 764—773).—The question of the validity of the principle of optical superposition has been examined by reference to the rotatory powers of the four meta-saccharins and of their strychnine, brucine,

and quinine salts. It is shown that the specific and molecular rotations may be satisfactorily represented as the algebraic sums of three constants corresponding with the active α-, γ-, and δ-carbon atoms. The calculated constants for the α- and γ-carbon atoms are very nearly the same for all the salts, but differ considerably from the α- and γ-constants for the saccharins themselves. This is quite in accordance with the fact that ring structure is present in the saccharins, whilst the salts are characterised by chain structure. The sum of the activities of the δ-carbon atom and the active base remains constant for the four salts corresponding with each of the three bases, but changes its value with the nature of the alkaloid.

By using the average values of the constants and calculating the specific rotations of the twelve salts, it is found that the average differences between the calculated and observed rotations are $0 \cdot 94°$ for the strychnine salts, $0 \cdot 25°$ for the brucine salts, and $0 \cdot 22°$ for the quinine salts.

Reference is made to other recorded data which afford evidence of the validity of the principle of optical superposition.

H. M. D.

Action of Light-rays on Organic Compounds and the Photosynthesis of Organic from Inorganic Compounds in Presence of Inorganic Colloids. BENJAMIN MOORE and T. A. WEBSTER (*Proc. Roy. Soc.*, 1918, [*B.*] **90**, 168—186).—In the formation of formaldehyde from carbon dioxide in light in the presence of an inorganic catalyst, it is shown that the action depends, not only on the specific character of the catalyst, but also on its state of aggregation. Exposure of formaldehyde solutions to light lead to the formation of condensation products which reduce Benedict's solution. The relationship between the osmotic energy and thermochemical relations in reversible reactions of this description is discussed. The authors also discuss generally the formation of formaldehyde by phytochemical decomposition of more complex substances.   S. B. S.

The Parent of Actinium. FREDERICK SODDY and JOHN A. CRANSTON [and, in part, ADA HITCHINS] (*Proc. Roy. Soc.*, 1918, [*A.*] **94**, 384—404).—The history of the long search for the parent of actinium, and of the various theories that have been framed to connect it with uranium, is dealt with in full. The present work was undertaken to test the hypothesis that actinium is produced from " eka-tantalum," the missing element between uranium and thorium in the Periodic Table, by its disintegration in a slow α-ray change, giving actinium. Eka-tantalum is probably the product of uranium-Y, discovered by Antonov (A., 1911, ii, 844; 1914, ii, 17), and it should be isotopic with uranium-X_2 or brevium.

It was found that uranium-X_2 could be effectively separated from uranium-X_1, isotopic with thorium, by distillation at a dull red heat in chlorine charged with carbon tetrachloride vapour, the uranium-X_2 volatilising. The attempt was made to separate eka-

tantalum from pitchblende similarly. About 500 grams of a very pure Indian pitchblende (U_3O_8 86%, PbO 11·9%, ThO_2 1·9%, SiO_2 0·6%) similarly treated gave three sublimates, the first after twenty-two hours, the second after ninety hours further, and the last [prepared by (Miss) A. Hitchins] after six hours at a much higher temperature. These sublimates were kept under observation for the growth of actinium, from which they were initially free. The presence of actinium was tested for by means of its characteristic active deposit. The second sublimate, in the course of one thousand days, produced a quantity of actinium twenty times greater than could be with certainty detected. So far as can yet be seen, the rate of growth of actinium appears to be linear with the time, pointing to a direct production. The other preparations have remained free from actinium. Another preparation, from Joachimsthal pitchblende, treated similarly, gave a sublimate also giving actinium with time. For the second sublimate from Indian pitchblende, the attempt was made to compare the quantity of actinium present after 2·5 years with that in the originating pitchblende. The amount of actinium present was found to be the same as that in 0·25 gram of the pitchblende. On the assumptions (1) that the actinium is produced in a direct change, (2) that the sublimate contained all the parent of actinium present in the original mineral, the period of average life of actinium is calculated to be 5,000 years. The quantitative measurement by radio-active methods of minute quantities of actinium by means of its emanation and active deposit presents difficulties which have not been completely overcome. The work supports the theory of the origin of actinium, referred to at the beginning, but does not finally establish it to the exclusion of all other possible modes of origin.

F. S.

Mobilities of Ions in Air, Hydrogen, and Nitrogen.

KIA-LOK YEN (*Proc. Nat. Acad. Sci.*, 1918, **4**, 91—97).—The mobilities of the positive and negative ions in air, hydrogen, and nitrogen have been measured at various pressures and for widely different potentials. The results show that the mobility varies inversely as the pressure, and that the product of these quantities is independent of the strength of the field in the case of both positive and negative ions. The results are discussed with reference to the constitution of the ions, and the author contends that they afford support for the view that the ions consist of a single atom or molecule, as opposed to the cluster hypothesis according to which an ion is supposed to consist of a relatively large group of satellite molecules. The fact that the mobility of the negative ions is in all cases greater than that of the positive ions can be readily explained in terms of the simple ion hypothesis when the relative magnitude of the forces acting between neutral molecules and ions of opposite sign is taken into account. This attractive force is greater for the positive ion, and, in consequence, the effective mean free path of the positive ion is less than that of the negative ion.

The reduced mean free path involves a diminution in the mobility of the positive ions as compared with that of the negative ions.

H. M. D.

Mobilities of Ions in Vapours. KIA-LOK YEN (*Proc. Nat. Acad. Sci.*, 1918, **4**, 106—109).—The mobilities of the positive and negative ions in sulphur dioxide, acetaldehyde, ethyl chloride, ethyl alcohol, pentane, acetone, ethyl acetate, ethyl iodide, and methyl iodide have been measured at various pressures. The mean values obtained show that the mobility of the negative ion is slightly greater than that of the positive, except in the case of ethyl iodide, for which the observed values are the same. The ratio of the mobilities of the oppositely charged ions in these vapours is much smaller than the ratio found in the case of air, hydrogen, and nitrogen, and is quite in accordance with the assumption that the ions are simple in type (compare preceding abstract).   H. M. D.

The Distribution of Radioactive Gases in the Free Atmosphere. VICTOR F. HESS and WILHELM SCHMIDT (*Physikal. Zeitsch.*, 1918, **19**, 109—113).—From the point of view of present knowledge of the interchange going on in the free air by virtue of the random molecular motion, the law for the distribution with height of a radioactive gas in the atmosphere and the comparison of the amount at any altitude with that present at the earth's surface have been worked out. The calculated values agree with such observations as have been made for the radium emanation, so far as the order of magnitude is concerned. The calculated values, for the height in which the quantity of the radioactive material per gram of air is reduced to half the value at the surface, are:

Radium emanation and its short-lived products, about 1200 metres.

Radium-D and subsequent products, uniform up to 10 kilometres.

Thorium emanation and thorium-A, 2 to 3 metres.

Thorium-B and subsequent products, 100 to 150 metres.

Actinium emanation and actinium-A, 0·5 to 1 metre.

Actinium-B and subsequent products, 10 to 20 metres.

The total quantity of radium emanation in the whole atmosphere is estimated as between 1·6 and 2·3 × 10^7 Curies.   F. S.

Attempted Separation of Isotopic Elements by means of Fractional Diffusion. H. LACHS, M. NADRATOWSKA, and L. WERTENSTEIN (*Compt. rend., Soc. Sci. Warsaw*, 1917, **9**, 670—672; from *Chem. Zentr.*, 1918, i, 416).—In an attempt to separate the isotopes U_1 and U_2 by the fractional diffusion of a solution of uranyl nitrate, no difference was observable between the radioactivity of the diffusate and of the original substance. If there is any difference between the diffusion coefficients of the two isotopes, it cannot be greater than 1·5%.   D. F. T.

Can the Production of Electricity by Organic Substances and Living Tissue be Explained by known Thermodynamic Laws? R. BEUTNER (*Zeitsch. Elektrochem.*, 1918, **24,** 94—100).—Polemical against Baur and Kronmann (A., 1917, ii, 231). It is shown that the production of the current in two-phase liquid elements can be explained thermodynamically, and, consequently, the production of the biological current can also be explained in the same way. It is claimed that the absorption theory of Baur, which is put forward to take the place of the thermodynamic theory, is therefore superfluous, and, furthermore, unproved.　　　　　　　　　　　　　　　　　　　　J. F. S.

Can the Production of Electricity by Organic Substances and Living Tissues be Explained by known Thermodynamic Laws? EMIL BAUR (*Zeitsch. Elektrochem.*, 1918, **24,** 100—101).—Polemical, an answer to Beutner (see preceding abstract).　　　　　　　　　　　　　　　　　　　　J. F. S.

Potentials of the Bismuth–Bismuth Oxychloride and the Copper–Cuprous Chloride Electrodes. ARTHUR A. NOYES and MING CHOW (*J. Amer. Chem. Soc.*, 1918, **40,** 739—763).— The normal potentials have been derived from measurements of the $E.M.F.$ of cells formed by combination of the bismuth oxychloride and cuprous chloride electrodes with the hydrogen electrode and with each other. The mean values obtained for the normal potential of the bismuth oxychloride electrode are -0.1635, -0.1599, and -0.1563 volt at $15°$, $25°$, and $35°$ respectively. The corresponding values for the cuprous chloride electrode are -0.1263, -0.1200, and -0.1132 volt respectively.

From the temperature coefficients of the electrode potentials, the authors have calculated the heat changes accompanying the chemical reactions. The results are expressed in the equations

$$3/2H_2 + 3CuCl = 3Cu + 3\overset{+}{H} + 3\overset{-}{Cl} + 21570 \text{ cal.}$$

$$3/2H_2 + BiOCl = Bi + H_2O + \overset{+}{H} + \overset{-}{Cl} + 18500 \text{ cal.}$$

$$Bi + 3CuCl + H_2O = 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl} + 2825 \text{ cal.}$$
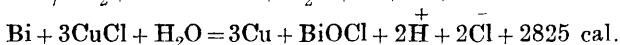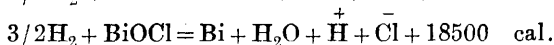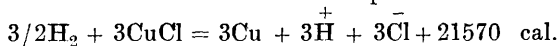
By measuring directly the heat of the reaction between metallic tin and bismuth oxychloride, and also of the reaction between tin and cuprous chloride in presence of dilute hydrochloric acid, the value found for the last of the above reactions is 7390 cal., which is very much larger than that indicated by the potential measurements. The discrepancy has not yet been accounted for.

The equilibrium corresponding with the equation $Bi + 3CuCl + H_2O \rightleftharpoons 3Cu + BiOCl + 2\overset{+}{H} + 2\overset{-}{Cl}$ has been determined by experiments at $75°$. The constant $K_{75} = [\overset{+}{H}]^2 . [\overset{-}{Cl}]^2$ has the value 2.10×10^{-3}.　　　　　　　　　　　　　　　　　　　　H. M. D.

Electrical Endosmose. II. T. R. BRIGGS, H. S. BENNETT, and H. L. PIERSON (*J. Physical Chem.*, 1918, **22,** 256—272). Compare A., 1917, ii, 236).—An improved form of electro-osmometer

is described which consists essentially of a horizontal tube containing the diaphragm, in close proximity to which are the electrodes, which pass through vertical side tubes which permit of the escape of gases generated during the passage of the current. The anode and cathode compartments are also connected through a narrow tube which contains an air bubble. This tube is provided with a scale, and the rate at which the bubble moves along the tube affords a measure of the electro-endosmotic flow.

Measurements have been made which show the dependence of the effect on the applied potential difference, the temperature, and on the nature of the diaphragm and of the dissolved electrolyte.

The rate of endosmotic flow is proportional to the applied difference of potential. For a given potential, it increases with rise of temperature, the rate of increase being somewhat smaller than that of the fluidity.

The results obtained in the investigation of dilute acid and alkaline solutions confirm the observation, made by Perrin, that the direction of flow undergoes reversal on passing from an acid to an alkaline solution. With a carborundum diaphragm, the isoelectric point was found to correspond with a very slightly acid solution. Sharp reversals were also obtained with alundun and also with diaphragms of gelatin and agar jellies. With powdered glass, no reversal was obtained.

Observations made with various copper salts are also recorded, and the bearing of the electro-endosmotic effects on the electrical and adsorption theories of dyeing is discussed in reference to some experiments made with acid and basic dyes.　　　H. M. D.

The Abnormality of Strong Electrolytes. I. Electrical Conductivity of Aqueous Solutions. JNANENDRA CHANDRA GHOSH (T., 1918, **113**, 449—458).—The fact that the ionisation of strong electrolytes, as measured by the electrical conductivity or osmotic methods, does not vary with the dilution in accordance with the requirements of the law of mass action, is supposed to be due to the invalidity of the fundamental idea underlying the Arrhenius ionic theory. According to the author, strong electrolytes are completely ionised, and there is no question of an equilibrium between ions and unionised molecules. The relations between the ions are determined solely by the electrical forces acting between the ions, and the interior of a solution of a strong electrolyte is characterised by a certain potential, A, which affords a measure of the work which is required to remove the ions from the influence of their mutual attractive forces. By application of the kinetic theory, it may be inferred that ions become "free" when their velocity exceeds a certain critical value. The fraction of the free ions is equal to $e^{-A/nRT}$, in which n is the number of ions formed from a molecule of the electrolyte. Denoting the Avogadro number by N, then the number of free ions is $nNe^{-A/nRT}$. At infinite dilution $A=0$, and the number of free ions $=nN$. From this follows $A = nRT\log_e\mu_\infty / \mu_v$ (1).

Assuming that the marshalling of the ions in solution corre-

sponds with the arrangement of the atoms in the crystallised electrolyte, and that the component ions form a completely saturated electrical doublet, it is possible to calculate A from the charge E carried by the ions and r their distance apart. In the case of a binary electrolyte, the equation is $A = E^2/Dr$, where D is the dielectric constant of the solvent medium and $r = \sqrt[3]{v/2N}$ (2). From equations (1) and (2), the value of μ_v may be calculated for varying dilutions, and it is shown that the calculated values are in close agreement with those found by experiment between $v = 10$ and $v = 5000$. The agreement is also good in the case of ternary electrolytes. For bi-bivalent electrolytes, agreement is found for dilutions between $v = 10$ and $v = 100$, but at $v = 1000$ the observed conductivities are much greater than those calculated from the author's formula. The discrepancy is said to be due to hydrolysis.

On account of the diminution of the dielectric constant with rise of temperature, the value of μ_v/μ_∞ should decrease. The observed diminution for potassium chloride at 100° is shown to be in satisfactory agreement with that calculated from the author's formula.   H. M. D.

"The Magnetic Properties of Zinc Blende and some other Minerals." F. STUTZER, W. GROSS and K. BORNEMANN (*Metall und Erz*, 1918, **15**, i, 1—9).—A method is described for measuring the magnetic susceptibility of paramagnetic minerals such as zinc blende, and a list of values of this constant given for fifty-three samples.   F. C. T.

Theoretical and Experimental Investigation of the Thermal Conductivity of Mixtures of Gases. SOPHUS WEBER (*Ann. Physik*, 1917, [iv], **54**, 481—502).—The theory of the thermal conductivity of gas mixtures is discussed in reference to the experimental data recorded in the literature. New measurements have been made for mixtures of hydrogen and carbon dioxide and of nitrogen and argon, and it is found that the results may be satisfactorily represented by the formula
$$K = K_1/(1 + A\,p_2/p_1) + K_2/(1 + B\,p_1/p_2),$$
in which K_1 and K_2 are the thermal conductivities of the constituent gases, p_1 and p_2 the partial pressures of the components in the mixture for which the conductivity is K, and A and B are empirical constants. These constants differ very widely from those which are indicated by theory. In the case of mixtures of hydrogen and carbon dioxide, the values of the constants indicated by theory are $A = 1{\cdot}01$ and $B = 2{\cdot}56$, whilst the empirical values which satisfy the experimental results are $A = 2{\cdot}70$ and $B = 0{\cdot}40$. For mixtures of nitrogen and argon, the empirical values are $A = 1{\cdot}07$ and $B = 0{\cdot}95$. Since the constants are in this case nearly equal, it follows that the thermal conductivity of mixtures is approximately given by the mixture formula, according to which
$$K = K_1 \cdot p_1/(p_1 + p_2) + K_2 \cdot p_2/(p_1 + p_2).$$ H. M. D.

Theory of Specific Heats. CARL DRUCKER (*Zeitsch. Elektrochem.*, 1918, **24**, 83—84).—Polemical, in which the author

criticises the method employed by Jankowsky (this vol., ii, 59) in deducing certain relationships for the specific heat of gases. The deductions drawn from the mathematical expressions are also criticised.   J. F. S.

Specific Heat at Low Temperatures. IV. Measurements of the Specific Heat of Liquid Hydrogen. Preliminary Results on the Specific Heat of Solid Hydrogen and on the Heat of Fusion of Hydrogen. W. H. KEESOM and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1000—1004. Compare A., 1916, ii, 371).—The apparatus previously described has been used in the determination of the specific heat of liquid hydrogen. According to the most complete of several series of measurements, the atomic heat increases from 1·75 at 14·82° (abs.) to 2·26 at 20·11°.

The data obtained for solid hydrogen gave a mean value of 0·64 at 12·55° for the atomic heat, and for the latent heat of fusion the value 15 was obtained as the mean of two experiments.

                                                    H. M. D.

Specific Heats of Lead–Antimony Alloys. R. DURRER (*Physikal. Zeitsch.*, 1918, **19**, 86—88).—Within the limits of experimental error, the specific heat of alloys of lead and antimony agrees with that calculated from the specific heats of the components by the simple mixture rule. The specific heat (between 0° and 100°) is actually represented by the equation

$$S = 0·04965 - 0·0001884\ p,$$

where p is the percentage of lead in the alloy. The freezing-point diagram for this pair of metals shows that there are two curves meeting in a eutectic point at 249°.   H. M. D.

Atomic Heats of Tungsten and Carbon at Incandescent Temperatures. A. G. WORTHING (*J. Franklin Inst.*, 1918, **185**, 707—708).—Many of the theories, based on the quantum hypothesis, for explaining the variation of the atomic heat with temperature, lead to the value 5·95 cal. per gram-atom degree as the upper limit for this quantity. With the object of testing these conclusions, the atomic heats of tungsten and carbon have been determined at high temperatures. The elements were used as filaments contained in closed globes at constant pressure; the heating was electrical, and the rate of cooling was determined by means of a potentiometer and a pendulum which operated switches at various points in its path. In the case of tungsten, the atomic heat is shown to vary almost lineally from 6·25 cal. per gram-atom degree at 1200° to 7·35 cal. per gram-atom degree at 2400°. That is, at these temperatures it has an atomic heat which is considerably above the theoretical maximum value. 5·95. In the case of carbon, the value varies from 5·35 at 1200° to 6·05 at 2000°.

                                                    J. F. S.

Melting Point Apparatus. J. C. HIBBERT and W. F. THOMPSON (*Analyst*, 1918, **43**, 216).—A test-tube, 7 inches by 1·4

                                                    12*

inches, is supported in a clamp and closed by a cork; the thermometer is attached to a glass tube passing through the cork. The stirrer also passes through a slot in the cork and is supported by rubber rings connected with a bent wire fixed to the clamp stand. The burner is provided with a glass wind-screen.   W. P. S.

Sulphur as a Cryoscopic Solvent. E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, **102**, 201—214).—In spite of the facility with which it undergoes transformation into allotropic modifications, sulphur can be successfully used as a cryoscopic solvent if certain conditions are fulfilled. Soon after having been melted, the freezing point of sulphur is about 119°, but after it has been kept for some hours at a temperature just above its melting point, the freezing point falls to 114·5°, and in this condition the sulphur is suitable for cryoscopic determinations. The apparatus and method employed have been previously described (A., 1897, ii, 88).

The cryoscopic constant of sulphur was determined by means of a number of organic compounds, bromoform (229·3), phenylthiocarbimide (226·6), naphthalene (211·4), diphenyl (208·4), thymol (206·4), quinoline (205·7), β-naphthol (205·2), and aniline (201·8), the mean value of K being 213. The latent heat of fusion w, calculated from van't Hoff's equation, is 14·1 gram cal., a value somewhat higher than that determined experimentally for monoclinic sulphur. In accordance with its low dielectric coefficient, 4·0, sulphur shows no dissociating power. Substances of an acidic character like p-cresol and α-naphthoic acid show a tendency to associate to double molecules, the value of K falling with increasing concentration.

The "natural" m. p. of sulphur, 114·5°, corresponds with a content of about 3·6% S_μ. The observation of A. Smith (A., 1907, ii, 20), that the attainment of a steady m. p. by sulphur is delayed by sulphur dioxide and accelerated by ammonia, is confirmed. Organic compounds of a neutral or acidic character resemble the former, whilst basic substances, such as pyridine and aniline, resemble ammonia in their behaviour. These substances act catalytically by delaying or accelerating the formation of S_μ, which may itself, however, be formed from S_π.

Arsenic trisulphide in sulphur has the simple molecule As_2S_3, but tends to polymerise with increasing concentration. Selenium tetrachloride shows a molecular weight of half the normal value, and this is attributed to the formation of selenium and sulphur monochlorides.   ,   E. H. R.

Measurement of Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature. P. G. CATH and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 991—999. Compare A., 1914, ii, 27).—An improved form of helium gas thermometer is described, and an account is given of the apparatus and

methods employed in the further measurement of the vapour pressure of liquid hydrogen at temperatures ranging from the boiling point to the critical point. H. M. D.

The Saturated Vapour Pressures of Tetratomic Substances. E. Ariès (*Compt. rend.*, 1918, **166**, 802—805).— On the basis of the vapour pressures of ammonia given in the *Recueil de Constantes physiques*, the formula for the saturated vapour pressures of tetratomic substances is given as $\Pi = \tau^{17/6} Z / x$, where $x = [1 + (1 - \tau)(0{\cdot}84 - \tau)/(\tau^2 + 1)]\tau^{11/6}$. Whilst the observed values for phosphorus trichloride are in fair agreement with those calculated from this formula, the agreement is not so good in the case of acetylene. W. G.

The Association of Organic Compounds in Benzene and Alcohol Solution as determined by the Vapour Pressure Method. William Ross Innes (T., 1918, **113**, 410—435).—The vapour pressures of benzene and ethyl alcohol when mixed with varying quantities of non-volatile substances have been measured at certain fixed temperatures. From the experimental data, the author has calculated the apparent molecular weight of the non-volatile substance by making use of the equation for Raoult's law. If g grams of the substance of molecular weight m are dissolved in G grams of the volatile solvent of molecular weight M, and the vapour pressures of the pure solvent and solution are p and p', then this equation may be written in the form $m' = gMp'/G(p - p')$, where m' is the apparent molecular weight of the non-volatile solute. The results obtained are shown by means of curves, in which m'/m is plotted as a function of the percentage molecular concentration of the solute.

When benzene is used as solvent, the curves obtained may be divided into groups. In one of these, the substances have values of m'/m which differ but little from unity even when the molecular concentration of the substance is very large. Acids and oximes form a group showing considerable association. In the case of formanilide and acetanilide, the value of m'/m increases rapidly with the concentration, and a maximum appears to be reached. Ethyl tartrate is extremely abnormal in that very high values are found for m'/m, which reaches a maximum when the percentage molecular concentration is about 50 and diminishes rapidly at higher concentrations.

In alcohol as solvent, four substances were examined, and all gave values of m'/m which increase with the concentration. In the case of azobenzene, which is readily soluble in hot alcohol, the association factor seems to increase continuously with the concentration. The value of m'/m obtained for this substance in 60% solution is about 6·0.

The theoretical interpretation of the results is discussed in some detail, and in this connexion attention is directed to results obtained for mixtures of sulphuric acid and water (compare T.,

1904, **85**, 1345), according to which the apparent molecular weight is very small and decreases rapidly with increasing concentration.

H. M. D.

Heats of Dilution and their Variations with Temperature.

FRANK R. PRATT (*J. Franklin Inst.*, 1918, **185**, 663—695).—The heat of dilution of solutions of a large number of salts has been· determined at a series of temperatures with the object of testing the validity of the expression $dl/d\theta = -dH/dm$, in which l is the heat of dilution, θ the temperature, m the mass of the solution, and H the heat capacity of the system. The measurements were made by the method of constant flow, in which two streams, of solution and water respectively at the same temperature, were allowed to mix continuously in a Dewar vessel at constant temperature. Solutions of sodium chloride, potassium chloride, barium chloride, strontium chloride, ammonium chloride, sodium hydroxide, potassium hydroxide, sodium nitrate, potassium nitrate, barium nitrate, strontium nitrate, and ammonium nitrate were used. The results indicate that in a general way the above formula is true. The discrepancies are discussed. A further series of measurements was made with the following non-electrolytes: resorcinol, dextrose, sucrose, catechol, quinol, mannose, and ethyl alcohol. The chief point of interest arising from these experiments is that for non-electrolytes H is constant for all concentrations; on the whole, the results here are in general agreement with the above formula.

J. F. S.

Possibility of Calculating the Properties of Liquids and Vapours.

JOHANNES GEISSLER (*Zeitsch. Elektrochem.*, 1918, **24**, 101—113).—A theoretical paper in which the author has shown that for the four substances fluorobenzene, benzene, ethyl ether, and carbon tetrachloride there is a region in which the physical properties can be represented by straight lines, and that within the limits of this area the physical properties can be calculated. Methods are worked out for calculating (1) the molecular volume of the saturated vapour from that of the liquid, (2) the molecular volume of a liquid from the temperature, (3) the coefficient of expansion of a liquid from the temperature, (4) the vapour pressure of a liquid from the temperature, (5) the change of vapour pressure per degree at a given temperature, (6) the latent heat of vaporisation of a liquid at a given temperature. The calculated and experimental values are compared, and it is shown that whilst there is good agreement in many cases, there are also divergences. The latter are attributed to the use of data obtained in a region removed from the limited region mentioned above, or from data in the neighbourhood of the freezing point.

J. F. S.

Atomic and Molecular Numbers.

HERBERT STANLEY ALLEN (T., 1918, **113**, 389—396).—A short account is given of the significance of the atomic number in connexion with the periodic

classification of the elements. The atomic numbers of analogous elements differ by eight or a multiple of eight, or in some cases by a number which is two units greater than one of the foregoing. The reason for these variations from the rule of eight is the presence of three elements in group VIII of the periodic table.

Molecular numbers of analogous compounds show similar relations. In reference to organic compounds, it is pointed out that the molecular number for the group ·CH_2· is eight, and the rule of eight is consequently of wide application in organic chemistry. It is probable that many properties of chemical compounds will be found to depend on the values of the molecular numbers.

H. M. D.

Modified Mercurial Viscosimeter for Determining the Viscosity of Volatile Liquids. F. M. LIDSTONE (*J. Soc. Chem. Ind.*, 1918, **37**, 148—149т).—In the apparatus described, an attachment is provided by means of which an equal excess pressure may be applied above and below the moving column of liquid in the viscometer. This prevents the formation of a cushion of vapour between the mercury and the volatile liquid under examination, but does not interfere with the usual constants of the instrument. W. P S.

The Viscosity of Liquefied Gases. X. The Viscosity of Liquid Hydrogen. J. E. VERSCHAFFELT (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 986—990. Compare A., 1917, ii, 408).—From observations on the time of oscillation of a specially designed oscillatory system immersed in the liquid hydrogen, the viscosity at 20·4° (abs.) has been found to be $\eta = 0·000130$, with an estimated accuracy of about 1%. A preliminary determination of the viscosity of the saturated vapour at this temperature (vapour pressure = 76·9 cm.) gave $\eta = 0·000010$. H. M. D.

Solubility Measurements. STEWART J. LLOYD (*J. Physical Chem.*, 1918, **22**, 300—302).—The measurements recorded were made incidentally in connexion with other work. The solubility of sulphur dioxide in benzene, toluene, nitrobenzene, *o*-nitrotoluene, and acetic anhydride was measured at various temperatures. At 20°, the solutions saturated at 756—760 mm. contain the following amounts in grams per litre: toluene, 236·0; nitrobenzene, 267·4; *o*-nitrotoluene, 236·0; acetic anhydride, 106. The solubility of aluminium chloride in carbon tetrachloride decreases from 0·74 at 4° to 0·06 gram per litre at 34°; in chloroform, from 1·00 at 0° to 0·72 at 25° and 0·65 at −15°. The solubility of barium chloride in nitrobenzene increases from 0·167 at 20° to 0·40 at 100°, and that of benzoic acid in ethyl acetate from 8·0 grams per litre at −6·5° to 37·7 at 21·5° and 95·7 at 75°. H. M. D.

Reactions between Solid Substances. ·LESLIE HENRY PARKER (T., 1918, **113**, 396—409. Compare T., 1914, **105**, 1504). —The rate at which certain solid substances react together has

been examined systematically by observations at various temperatures up to and above the fusion temperature. The pairs of substances investigated were sodium carbonate and barium sulphate, silver nitrate and sodium carbonate, cuprous chloride and sodium carbonate. In all cases, the mixtures were made from carefully dried substances. Although the results obtained show clearly that reaction takes place below the fusion temperature, and that the rate of the reaction between the solids increases continuously with rise of temperature, there is in all cases a very marked increase in the velocity at the temperature of fusion. The ratio of the velocity in the fused mixture to that at the highest temperature in the solid state varies in the three cases examined. It is immeasurably large in the mixture containing barium sulphate, is equal to about 150 for the mixture containing silver nitrate, and to about 20 for the mixture containing cuprous chloride.

The results seem to show that the liquid state per se has an influence on the rate of interaction, which influence is to be distinguished from that of temperature. The fact that shearing stresses give rise to reactions between solid substances does not seem as yet to be completely explained, and it is suggested that such stresses produce changes of state in the surface layers which are equivalent to that produced by fusion.   H. M. D.

Xanthic Acids and the Kinetics of their Decomposition. I. HANS VON HALBAN and WALTER HECHT (*Zeitsch. Elektrochem.*, 1918, **24**, 65—82. Compare A., 1913, ii, 312).—The rate of decomposition of xanthic acid [ethyl hydrogen dithiocarbonate, $OEt \cdot CS \cdot SH$] and methyl hydrogen dithiocarbonate in water at $0°$ has been studied. The solubility of these substances in water was first determined, and found to be at $0°$: xanthic acid, $0 \cdot 02$ mol. per litre; methyl hydrogen dithiocarbonate, $0 \cdot 05$ mol. per litre. The rate of decomposition was determined by dissolving a known amount of the sodium salt of the acid in question in water, and, when the solution had reached $0°$, liberating the acid with a slight excess of hydrochloric acid, then after a measured interval of time neutralising with a cooled solution of sodium hydrogen carbonate and titrating with a $0 \cdot 02N$-iodine solution. It is shown that, contrary to the behaviour of solutions in organic solvents, the velocity constants in the present case, when calculated on the basis of a unimolecular reaction, decrease rapidly with decreasing concentration; the decomposition is positively catalysed by hydrogen ions. This leads to the assumption that both the undissociated molecules and the ions take part in the reaction. On the basis of this assumption, the dissociation constants of the acids were calculated, and found to be independent of the dilution, a fact which confirms the assumption. At $0°$, the dissociation constant for methyl hydrogen dithiocarbonate is found to be $0 \cdot 034$, and that for xanthic acid $0 \cdot 030$. The addition of sulphates (Na, Mg. NH_4) to the decomposing xanthic acids in water solution strongly retards the action; for example, $0 \cdot 25N$-magnesium sulphate reduces the velocity of decomposition to one-third of the original value, and $3N$-ammonium

sulphate reduces it to one-sixth. A few velocity measurements have been made in ethyl alcohol, methyl alcohol, propyl alcohol, amyl alcohol, and benzyl alcohol solutions to complete the data published in an earlier paper (*loc. cit.*). Measurements were made at 0° on the partition of xanthic acid between water and carbon disulphide, chloroform, nitrobenzene, light petroleum, benzyl alcohol, and amyl alcohol respectively. It is shown that the dependence of the partition coefficient on the dilution is in accord with the dissociation constant calculated from the velocity values. The absorption spectrum of solutions of xanthic acid in light petroleum, 0·5N-ethyl alcohol in light petroleum, and in diethyl ether was measured, but although the rate of decomposition is very different in the different solvents, no difference could be observed in the absorption curves. Benzyl hydrogen dithiocarbonate was prepared from the potassium salt. This substance is a solid, m. p. 29°, and when quite pure may be kept for several hours, and in non-hydroxy-solvents has a normal molecular weight. The solubility and rate of decomposition have been determined in twelve solvents. The saturated solution at 0° has the following concentration in these solvents: hexane 0·224N, light petroleum 0·316N, methyl alcohol 0·36N, acetic acid 0·41N, nitromethane 1·49N, acetonitrile 3·26N, carbon disulphide 3·70N, acetone 3·41N, diethyl ether 2·93N, benzene 3·33N, ethyl bromide 3·88N, and nitrobenzene 3·15N. The van't Hoff velocity constant was calculated from the data, and these values, as well as those for xanthic acid, show that the catalytic influence of the solvent is not removed by the van't Hoff calculation.   J. F. S.

Hydrolysis of Ethyl Citrate and the Ethyl Hydrogen Citrates. JULIUS MEYER (*Zeitsch. Elektrochem.*, 1918, **24**, 84—85).—Polemical; the author claims that the work of Pinnow (this vol., ii, 103) is not the first case in which the hydrolysis of a tribasic ester has been studied, and then proceeds to criticise the results published by Pinnow.   J. F. S.

The Influence of Lipoids on the Rate of Reaction. M. SIEGFRIED (*Biochem. Zeitsch.*, 1918, **86**, 98—109).—Lecithin inhibits the transformation of the yellow mercuric iodide into the red variety, and also the reduction of ammoniacal silver nitrate by phenylhydrazine. The latter reaction should be carried out in the dark, and in the presence even of diffuse sunlight the inhibiting action of the lipoid is diminished.   S. B. S.

Ester Catalysis of γ-Lactones. HJALMAR JOHANSSON and HUGO SEBELIUS (*Ber.*, 1918, **51**, 480—485).—It has recently been shown that the hydrolysis of β-lactones to the hydroxy-acids is not catalysed by hydrogen ions (*Lunds universitets årsskrift*, 1916), and it appeared to be of interest, therefore, to determine directly whether the hydrolysis of γ-lactones, like the formation of them (compare Taylor and Close, A., 1917, ii, 253), is catalysed by acids.

For this purpose, the catalysis of the hydrolysis of γ-valero-lactone and γ-butyrolactone by nitric acid has been studied, the hydroxy-acid being titrated by means of barium hydroxide. It is found that in the case of γ-butyrolactone, with quantities of nitric acid represented by 9, 3, and 1, the time required for the production of the same percentage of hydroxy-acid is represented very nearly by 1, 3, and 9. The results with valerolactone are similar; H-ion concentration, 6 : 3 : 1 (roughly), and times, 1 : 3 : 6. The hydrolysis of γ-lactones is therefore a normal case of ester catalysis.

J. C. W.

Errors affecting Determinations of Atomic Weight. VII. Refinements in the Method of Weighing : Micro-balance : Application to the Atomic Weight of Helium and Hydrogen. PH. A. GUYE (*J. Chim. Phys.*, 1918, **16,** 46—61. Compare A., 1916, ii, 385, 386, 432, 435; this vol., ii. 40, 41).—The Taylor microbalance is discussed by the author and shown to be very suitable for the accurate determination of gaseous densities. Correct formulæ are developed for calculation of the density and molecular weight of gases from the experimental figures obtained in this way. These formulæ have been applied to the experimental figures obtained by Taylor (*Phys. Review*, 1917, **10,** 653), when the following values were obtained : normal litre of hydrogen weighs 0·089858 gram, molecular weight 2·0151; normal litre of helium weighs 0·17835 gram, molecular weight 3·9976. These values differ by about 10 per 10,000 from those calculated by Taylor. It is further shown that the Taylor microbalance appears to be susceptible of a few improvements, which are indicated by the author, and which, being made, give an instrument which will not only give the densities and molecular weights of gases with a precision at least equal to that of other methods, but which, with very small quantities of material, will give all the weighings necessary for the determination of atomic ratios. The great interest of the method lies in the fact that the determination of mass will resolve itself into the measurement of length, which is much more precise than weighing with weights, no matter how carefully calibrated.

J. F. S.

The Conception of the Chemical Element and the Phenomenon of Isotopy (Addendum). K. FAJANS (*Jahr. Radioaktiv. Elektronik*, 1918, **15,** 101—102. Compare A., 1917, ii, 566).—In further pressing the point of view that isotopic elements cannot be considered as one element, in Boyle's sense of undecomposability, an intimate mechanical mixture of isotopes is postulated as capable of being made and of existing as such in nature, which, since they can be imagined to be capable of being resolved into their constituents, if of different density, by the use of suitable fluids, cannot be regarded as undecomposable.

F. S.

Molecular Frequency and Molecular Number. III. Inorganic Compounds. Lindemann's Formula. H. STANLEY ALLEN (*Phil. Mag.*, 1918, [vi], **35**, 445—460. Compare this vol., ii, 163).—According to Lindemann, the characteristic molecular frequency of a compound is given by the formula $v = k \sqrt{T_s / M V^{\frac{2}{3}}}$, in which M is the molecular weight, V the molecular volume, and T_s the melting point of the compound on the absolute scale. Assuming $k = 3.08 \times 10^{12}$, this formula has been used to calculate the frequency for a large number of inorganic compounds. The results, which are arranged according to the periodic groups, afford further evidence of the validity of the relation $Nv = nv_A$ or $Nv = (n + \frac{1}{2})v_A$, according to which the product of the molecular number and the characteristic frequency is a simple multiple of the fundamental frequency v_A.

The fact that this relation holds for compounds which include elements belonging to all the different groups of the periodic system makes it appear very probable that the above equation is the expression of a relation which is of fundamental importance and characteristic of the solid state of matter. H. M. D.

Periodic System of the Elements. CHARLES P. STEINMETZ (*J. Amer. Chem. Soc.*, 1918, **40**, 733—739).—It is shown that the single, double, and quadruple periodicities which characterise the periodic system can be completely represented by a Riemann surface having two singular points at -40 and -130. Incidentally, it is pointed out that it is unjustifiable to assume that the functional relation between the properties of the elements and their atomic weights can be represented on a plane. H. M. D.

The Ductility of Metals and their Position in the Periodic System. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 247—254; from *Chem. Zentr.*, 1918, i, 509—510).—Lothar Meyer indicated that the ductile elements lie near the maxima and minima of the atomic volume curve. The author regards the occurrence of ductility as dependent on the formation of as many slip-planes as possible in the direction of main extension and the occurrence of movement with as little force as possible, and he uses the term ductility in the commonly accepted sense of capacity to be drawn into wire. Pairs of elements which form a continuous series of mixed crystals are regarded as isomorphous, so that by starting from a known crystal lattice it is possible to find many other examples of the same type. In the periodic system, a certain symmetry prevails in the crystalline form of the typical crystals, but is interrupted by the non-metallic elements of the carbon group. Elements with various crystalline forms are ductile. The ductility is not dependent on any definite space lattice, but probably on the occurrence of only one kind of atoms, between which no valencies are active, in the lattice of their crystals. If the valencies between the atoms of the lattice become active, as in the binary compounds of the metals, the formation of slip-bands is checked and the ductility disappears. D. F. T.

The Relationship of the Rare Earths to the Periodic System. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1918, **102**, 177—200).—The many attempts which have been made to fit the elements of the rare earths into existing groups of the periodic classification have all been unsatisfactory. There is only slight chemical and crystallographic justification for placing lanthanum in the third group and cerium in the fourth group, and in any case the valency of an element or the isomorphism displayed by certain of its salts serves as a very uncertain guide to its true relationship to other elements. The author agrees with Tammann that an element should show little or no chemical affinity for another element belonging to the same group; conversely, if two elements form a stable compound, they cannot belong to the same group. When this test is applied to the only rare earth element which is available in sufficient quantity for systematic study, cerium, it must be concluded that this element can belong to none of the ordinary groups of the periodic system. It forms binary compounds with metals of every group, with the exception of those of groups VI and VII, which have not been studied, and many of these compounds are remarkable for their great heats of formation and high melting points. In particular, cerium combines energetically with elements of groups III, IV, and V to form such compounds as $CeAl_2$ (m. p. 1460°), $CeAl_4$ (m. p. 1250°), Ce_2Sn (m. p. 1400°), and Ce_4Bi_3 (m. p. 1630°), whilst lanthanum also forms with aluminium a strongly exothermic compound, $LaAl_4$, of high melting point.

The new periodic law, based on the atomic numbers of the elements, requires the existence of sixteen elements between Ba(56) and Ta(73). Of these, fourteen rare earth elements are known, one being missing between Nd and Sm, and one between Lu and Ta. Whilst, therefore, the sixteen rare earth elements must form a continuous series with the remaining elements, they must form a special group by themselves.

A satisfactory representation of the position of the rare earth group in the family of elements is obtained in the following manner. The elements are arranged in order of atomic numbers on an ascending spiral, each turn of which corresponds with one short period of eight elements, elements belonging to the same group appearing vertically above one another. After passing Ba, the spiral changes its course and develops a subsidiary, smaller loop which, after making rather more than a complete turn, rejoins the original path of the spiral at Ta, group V. On this subsidiary loop are crowded the sixteen rare earth elements, which form a closely related family independent of the other groups situated on the main spiral. The elements La and Ce appear on the small loop in fairly close proximity to the vertical lines through groups III and IV respectively on the principal spiral, and this may account for certain properties shown by La and Ce in common with the elements of groups III and IV respectively. The rare earth elements themselves exhibit a certain periodicity in their basicity, magnetic properties, and in the solubility of their salts;

such periodicity or gradual change of properties is to be inferred from the form of the loop.

It is further suggested that the triads Fe,Co,Ni, Ru,Rh,Pd, Os,Ir,Pt also form three secondary loops on the principal spiral in place of elements belonging to group VIII. Each triad then forms a sub-group similar in character to the rare earth group, and homologous elements of the three triads appear on vertical lines parallel to the axis of the spiral. It is significant that the typical magnetic elements Fe, Co, Ni, and also the strongly paramagnetic elements Tb, Dy, and Ho, are all among those elements which do not conform to the normal course of the periodic system.   E. H. R.

Gas Generating Apparatus. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 64).—An apparatus for generating small quantities of hydrogen sulphide, carbon dioxide, hydrogen, etc., consists of a wide tube constricted at its middle so as to form two short, cylindrical bulbs; the upper bulb is provided with a tap and contains the ferrous sulphide or calcium carbonate, etc., whilst the lower bulb is connected by a glass tube to an acid reservoir at some height above the bulbs. The whole apparatus is made in one piece.   W. P. S.

Experimental Retort for Dry Distillation. F. E. COOMBS (*Met. and Chem. Eng.*, 1918, **18**, 425).—The retort consists of a cylinder of metal closed at the bottom. A similar cylinder, but of slightly larger diameter, so as to slide loosely over the retort, forms the lid, to which a bent delivery tube is fitted. The lid is secured to the retort by screws. The apparatus is placed in a bath of fused metal or sodium hydroxide, the level of which is below the top of the retort, which is now sealed by the liquid entering the annular space inside the lid. The contents of the retort can be distilled at a known and regulated temperature. The advantage claimed is accessibility for cleaning and charging.   H. J. H.

Extraction Apparatus for the Laboratory. CARL G. SCHWALBE and WALTER SCHULZ (*Chem. Zeit.*, 1918, **42**, 194).—A modification of the Besson extractor (A., 1916, ii, 26) in which no corks are employed and larger quantities (4—6 litres) of material may be extracted. The apparatus consists of a white metal cylinder in the upper part of which is fitted a wire ring which carries a fine cotton bag holding the material to be extracted. Above this bag is fitted a cylindrical condenser, through which a stream of water flows. The apparatus stands in a water-bath heated by a gas burner in the usual manner. All gas- and water-connexions are made of metal so as to ensure the safety of the apparatus.   A. B. S.

Simple Arrangement for Simultaneous Stirring and Filtration. FRITZ FEIGL (*Zeitsch. angew. Chem.*, 1918, **31**, i, 68).—To obviate the errors which occur when portions of a saturated solution at high temperatures are removed for solubility determinations, the author describes a combined stirrer and filter. The apparatus consists of a stout-walled, wide test-tube from which

the bottom has been removed, and on to the sides of which a number of glass vanes have been fastened. One end of the tube is covered with a piece of linen or hardened filter paper, the other end is inserted into a hole in a wooden pulley. The tube is then partly immersed in the saturated solution and rotated; the clear, saturated solution slowly filters into the tube, whence it can be withdrawn in suitable quantities. If a semipermeable membrane is substituted for the filter paper, the apparatus may be used to determine the velocity of diffusion of colloids below their coagulation temperature.

<div align="right">J. F. S.</div>

Grinding Glass Tips for Drop-weight Apparatus. EARL C. H. DAVIES (*J. Amer. Chem. Soc.*, 1918, **40**, 784—785).—For the measurement of surface tension by the drop weight method, it is necessary to prepare capillary tips of circular cross-section by grinding until the section is flat and smooth and the edges are perfectly sharp. To facilitate this, the author recommends the use of Wood's metal or other similar low melting alloy. The glass tube, made ready for the final adjustment of the tip, is lowered into the molten alloy, some of which is drawn into the capillary. The tube is left in position until the alloy has solidified, when the tip becomes firmly embedded in the alloy. The tube and alloy are then ground until the requisite sharp edge is obtained.

<div align="right">H. M. D.</div>

Willem Homberg. F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 602—605).—Further particulars of the life of the alchemist Homberg, including a reproduction of part of an autograph letter (compare this vol., A., ii, 164).

<div align="right">A. J. W.</div>

Anselmus Boëtius de Boodt. F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 628—671).—An account of the life and researches of the mineralogist de Boodt, who was born at Bruges in 1550, and died at the same place on June 21st, 1632.

<div align="right">A. J. W.</div>

Lecture Experiments for Demonstrating the Law of Multiple Proportions. F. EMICH (*Zeitsch. anal. Chem.*, 1918, **57**, 65—71).—Simple experiments are described, and comprise the estimation of oxygen in cupric and cuprous oxides by reduction with hydrogen, the formation of normal potassium tartrate and potassium hydrogen tartrate, and the gasometric estimation of carbon dioxide in sodium carbonate and sodium hydrogen carbonate.

<div align="right">W. P. S.</div>

Some Lecture Experiments with Silver Carbide. [Acetylide]. JOHN EGGERT and HANS SCHIMANK (*Ber.*, 1918, **51**, 454—456. Compare A., 1917, ii, 462).—The experiments are designed to show that pure silver carbide detonates very mildly in a vacuum, its bursting power under ordinary conditions being due to the rapid heating and expansion of the surrounding air.

<div align="right">J. C. W.</div>

Inorganic Chemistry.

The Relation of Iodine to Sulphur and Selenium. E. BECKMANN and C. PLATZMANN (*Zeitsch. anorg. Chem.*, 1918, **102**, 215—222).—The molecular weight of iodine determined cryoscopically in sulphur (K = 213) corresponds with I_2. Sulphur dissolved in iodine has the molecular composition S_8, but in the same solvent, selenium is dissociated into Se_2 and Se_1, although in organic solvents it exists as Se_8, and iodine, on account of its low dielectric constant, would not be expected to have dissociating properties. The freezing point of sulphur is raised by selenium, as is to be expected, since the two substances are isomorphous. On account of the sparing solubility of selenium in sulphur, experimental determinations were limited to concentrations up to 2·5% Se. Over this range, the elevation of the freezing point was approximately proportional to the concentration, and averaged 0·242° per 1% Se. It is concluded that in sulphur–selenium mixtures the latter is present as Se_8.

The depression of the freezing point of sulphur–selenium mixtures by iodine and diphenyl was determined. The cryoscopic constants of mixtures containing up to 1·58% Se were found to be practically equal to that of sulphur alone. On the assumption that the change of the freezing point of sulphur containing selenium and iodine is the algebraic sum of the elevation due to Se_8 and the depression due to I_2, the total effect was calculated and the result compared with the observed value for a number of concentrations. The agreement was generally satisfactory. There is no evidence of the formation of a compound between selenium and iodine, and the low molecular weight of selenium in iodine solution remains unexplained. E. H. R.

Action of Thionyl and Sulphuryl Chlorides on Sulphur and Phosphorus. H. B. NORTH and J. CLAUDE THOMSON (*J. Amer. Chem. Soc.*, 1918, **40**, 774—777).—Thionyl and sulphuryl chlorides were heated in sealed glass tubes with sulphur and phosphorus at temperatures ranging from 70° to 180°. Both chlorides react with sulphur at 150° to 180°, with the formation of sulphur dioxide and sulphur monochloride. Under similar conditions, the two chlorides react with both red and yellow phosphorus, with the formation of phosphorus trichloride, according to the equations
$3SO_2Cl_2 + 2P = 2PCl_3 + 3SO_2$, $4SOCl_2 + 2P = 2PCl_3 + 2SO_2 + S_2Cl_2$.
Prolonged heating tends to produce phosphorus pentachloride in accordance with the equations $PCl_3 + SO_2Cl_2 = PCl_5 + SO_2$, $3PCl_3 + 4SOCl_2 = 3PCl_5 + 2SO_2 + S_2Cl_2$, but these reactions are far from complete after heating for several hours at 160—180° in presence of considerable excess of the sulphuryl or thionyl chloride. H. M. D.

Oxidation of Sulphur Dioxide and Ammonia in the Presence of Platinum and Rhodium. P. WENGER and C. URFER (*Ann. Chim. anal.*, 1918, **23**, 97—104).—Maximum oxidation of sulphur dioxide takes place at 432° in the presence of platinum black, 96·8% of the dioxide being converted into sulphur trioxide. When rhodium black is used as the catalyst, the maximum oxidation (91·1%) occurs at 610°. In the case of ammonia, 97% is converted into nitric and nitrous acids by platinum black at 533° to 562°, whilst with rhodium black a maximum oxidation of 69·7% is attained at 662°.   W. P. S.

Synthesis of Ammonia at High Temperatures. II. EDWARD BRADFORD MAXTED (T., 1918, **113**, 386—389. Compare *ibid.*, 168).—Further observations on the combination of nitrogen and hydrogen at high temperatures have been made by passing the 1 : 3 mixture through a capillary tube fitted with platinum wire electrodes, between which sparks were made to pass by connecting the wires with an induction coil. When the distance between the electrodes is gradually reduced, the ordinary spark discharge is transformed into a small high-tension arc characterised by a continuous flame of high temperature. In experiments in which the rate of passage of the gas was kept constant and the size of the gap reduced, it was found that this was accompanied by a continuous increase in the percentage of ammonia formed. Similar results were obtained when the speed of the gas was controlled so as to give a constant time of contact. For a fixed width of gap, the percentage of ammonia was found to increase as the rate of flow of the gaseous mixture diminished. The results generally are in agreement with those obtained in the previous high-temperature measurements (*loc. cit.*).   H. M. D.

Synthesis of Nitrosyl Bromide. E. MOLES (*J. Chim. Phys.*, 1918, **16**, 3—10; *Anal. Fis. Quim.*, 1918, **16**, 377—385).—The author has examined the reaction of nitric oxide on bromine, and the nature of the resulting nitrosyl bromide, with the object of ascertaining whether this substance is suitable for use in the determination of the atomic weight of bromine by the method employed by Wourtzel (A., 1913, ii, 771) for chlorine with nitrosyl chloride. After a series of very careful experiments, it is found that the nitrosyl bromide produced always contains a slight excess of bromine, and consequently the compound is of no use for the purpose of determining atomic weights.   J. F. S.

Preparation of Carbon Tetrachloride from Carbon Disulphide and Chlorine. ISCO CHEMICAL Co. (U.S. Pats. 1260621 and 1260622).—Carbon disulphide containing free sulphur is treated with chlorine in the presence of a catalyst to form sulphur dichloride and carbon tetrachloride, and an additional quantity of carbon disulphide is then added to convert the sulphur dichloride into sulphur monochloride, with the formation of more carbon

tetrachloride. The product is treated with sufficient tin to convert the sulphur monochloride into sulphur, with the formation of stannic chloride, and, after separating the sulphur, water is added to hydrate the stannic chloride, and the carbon tetrachloride is recovered from the mixture by distillation. A. S.

Causticising of Potassium Carbonate. E. BELLONI (*Ann. Chim. Applicata*, 1918, **9**, 115—149).—The reaction between potassium carbonate and calcium hydroxide is reversible, and may be represented as a heterogeneous system in which there are two solid phases and one liquid phase containing variable proportions of the other components. From mathematical data based on the consideration of the formulæ of Bodländer and Lucas (A., 1905, ii, 634) and Le Blanc and Novotny (A., 1907, ii, 22), the following general isotherm for the conversion of an alkali carbonate into hydroxide by the action of calcium hydroxide has been deduced: $C^2_{KOH(NaOH)} C / C_{K_2CO_3(Na_2CO_3)} = a - a'\phi + a''\phi^2$, where C^2_{KOH} represents the concentration in gram-molecules of alkali hydroxide, $C_{K_2CO_3}$ the concentration of the alkali carbonate in the final solution, and ϕ the concentration of the carbonate in the initial solution. The constant K, which represents any given concentration giving stable equilibrium, is a definite function of ϕ to which the form may be given $K = a - a'\phi + a''\phi^2$. In the special case of the conversion of potassium carbonate into hydroxide at 100°, and for values of ϕ varying from 0 to 1·5 (that is, for solutions up to 3N), the equation assumes the form $C^2_{KOH} / C_{K_2CO_3} = 133\cdot20 - 127\cdot85\phi + 43\cdot50\phi^2$. The yield of potassium hydroxide obtainable from a solution of potassium carbonate of known concentration may be calculated by means of the equation $C_{KOH} = K(-0\cdot25 + \sqrt{0\cdot0625 + \phi/K})$. At equal molecular concentration of the solutions and under the same conditions of temperature, a greater yield of hydroxide is obtained from sodium carbonate than from potassium carbonate. The formation of a double carbonate of potassium and calcium at a given temperature is only possible at a single definite concentration, which at 100°, the temperature for technical preparation of hydroxide, is 61·78 grams per 100 c.c. This corresponds with a concentration much higher than is used in the manufacturing process. The temperature has a great influence on the velocity of the reaction, but does not affect the final stage of equilibrium. The results for equal concentrations, ϕ, at 80° and 100° were practically identical. [See also *J. Soc. Chem. Ind.*, 368A.] C. A. M.

Equilibria in Solutions containing Mixtures of Salts. I. The System Water and the Sulphates and Chlorides of Sodium and Potassium. W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1918, **10**, 344—347).—The conditions which govern the separation by fractional crystallisation of sodium and potassium salts were investigated by the aid of the phase rule diagrams for such solutions. The equilibrium conditions of the reversible reaction $3KCl + 2Na_2SO_4, 10H_2O \rightleftharpoons K_3Na(SO_4)_2 + 3NaCl + 20H_2O$ were studied, and the compositions of the solutions

saturated with one or more of these salts at 0°, 25°, 50°, 75°, and 100° were determined and plotted with respect to four axes representing sodium sulphate, potassium sulphate, potassium chloride, and sodium chloride. The diagrams represent the composition of all possible solutions which can be in equilibrium with these four salts, and with Glauber's salt and sodium potassium sulphate (glaserite), and indicate the stability of glaserite under widely varying conditions. [For details, see *J. Soc. Chem. Ind.*, 369A.]

<div align="right">W. F. F.</div>

Separation of Sodium and Potassium Chlorides and Sulphates by Fractional Crystallisation. W. C. BLASDALE (*J. Ind. Eng. Chem.*, 1918, **10**, 347—353).—The application of the principles described in the preceding abstract to the separation of mixed solutions is shown. Diagrams are given representing the composition of mixed solutions of (1) potassium chloride and sodium chloride, (2) potassium chloride and potassium sulphate, (3) potassium sulphate and sodium sulphate, (4) sodium sulphate and sodium chloride, and (5) mixtures of potassium salts with sulphates and chlorides of sodium and potassium. The diagrams are used to determine possible cycles of operation by which the various salts may be successively crystallised by evaporating and cooling at suitable temperatures. [For details, see *J. Soc. Chem. Ind.*, 369A.]

<div align="right">W. F. F.</div>

Production of a Stable Sodium Percarbonate. HENKEL & Co. (D.R.-P., 303556, 1915; from *Chem. Zentr.*, 1918, i, 497).—A compound, $2Na_2CO_3,3H_2O_2$, is obtained by the addition of sodium carbonate to an aqueous solution containing at least a sesquimolecular proportion of hydrogen peroxide; instead of sodium carbonate and hydrogen peroxide being taken as such, these substances may be produced in the solution by a suitable chemical change, for example, from sodium peroxide and sodium hydrogen carbonate.

<div align="right">D. F. T.</div>

The Calcium Arsenates. R. H. ROBINSON (*J. Agric. Res.*, 1918, **13**, 281—294).—Pure calcium hydrogen arsenate was prepared by pouring a calcium chloride solution slightly acidified with acetic, hydrochloric, or nitric acid into a sodium hydrogen arsenate solution similarly acidified. A heavy, voluminous precipitate was formed, which was washed by decantation, filtered, washed with hot water until free from chlorides, and dried at 100°. The washings were evaporated to a small volume, when crystals separated, and were washed and dried. Analysis showed both the powder and crystals to have the formula $CaHAsO_4,H_2O$. The water of crystallisation was lost at 175°.

Pure tricalcium arsenate was prepared by pouring an alkaline calcium chloride solution into an alkaline sodium hydrogen arsenate solution. A heavy, voluminous precipitate was formed, which was washed by centrifuging and decantation, and then filtered and

dried at 100°. Analysis agreed with the formula $Ca_3(AsO_4)_2,2H_2O$. The water of crystallisation was lost at 175°.

The specific gravity of the salts was determined by weighing in specially dehydrated absolute alcohol at 20°. The results were: for $CaHAsO_4,H_2O$, D_4^{20} 3·09; for $CaHAsO_4$, 3·48; for $Ca_3(AsO_4)_2,2H_2O$, 3·23; for $Ca_3(AsO_4)_2$, 3·31. Solubility was determined at 25° in a water-bath fitted with a revolving bottle-holder. One hundred grams of the solution contained in the case of $CaHAsO_4$ 0·3108 gram of the salt, and in the case of $Ca_3(AsO_4)_2$ 0·0133 gram.

J. H. J.

An Artificial Patina. OTTO GROTIAN (*Zeitsch. Elektrochem.*, 1918, **24**, 83).—The author describes a method of artificially producing an incrustation or patina on copper articles similar to that found on ancient bronzes. This film is produced by electrolysing a solution of copper sulphate between copper electrodes for three minutes with a current density of 1 amp./per sq. decimetre; the current is then interrupted and the cathode removed from the liquid. The anode is allowed to remain undisturbed in the liquid for twenty-four hours. The process is repeated several times, alternately passing the current for three minutes and leaving the anode for twenty-four hours. After several repetitions, the anode is removed and found to be covered with a beautiful bluish-green, non-crystalline patina, which cannot be removed by washing. On analysis, the film is shown to have the composition $CuO,3H_2O$.

J. F. S.

Mercury Fulminate and its Estimation. G. S. HEAVEN (*J. Soc. Chem. Ind.*, 1918, **37**, 143—147T).—Commercial mercury fulminate consists of a crystalline powder varying in colour from pale cream to dark brown; the largest crystals do not exceed 1 mm. in length, and these are more sensitive to impact than are the smaller crystals. A very fine powder, sifted through calico, fails to fire. Fulminate is soluble in alcohol, ammonia, pyridine, potassium cyanide solution, and in cold water, but is decomposed by hot water, alkali solutions, and thiosulphate solution. It does not inhibit the growth of fungi; *Tricoderma viride* and *Acrostalagmus albus Preuss* grow readily on bags containing fulminate, and even on the crystals themselves. The following method is recommended for the analysis of detonator composition containing fulminate, antimony sulphide, potassium chlorate, etc. A quantity of 0·3 gram of the sample is treated with 50 c.c. of $N/10$-thiosulphate solution, 0·3 gram of boric acid is added, the mixture is stirred for three minutes, and then titrated with sulphuric acid, using methyl-orange as indicator. The sulphuric acid is standardised previously against pure mercury fulminate. Any antimony sulphide which may be present is then collected on a filter, washed, dried, and weighed, or estimated volumetrically if the sample contains powdered glass. To the filtrate are added 100 c.c. of 10% ferrous sulphate solution containing 1 c.c. of free sulphuric acid,

the mixture is boiled for thirty minutes, the mercury sulphide collected, dissolved in aqua regia, the solution neutralised with ammonia, acidified with hydrochloric acid, and the mercury precipitated as sulphide. The mercury sulphide is collected and weighed, and the filtrate, containing reduced chlorate, is oxidised with nitric acid, and the chloride estimated volumetrically.

W. P. S.

Preparation of Inorganic Stannichlorides. J. G. F. DRUCE (*Chem. News*, 1918, **117**, 193—196).—A number of stanno- and stanni-chlorides of uni- and bi-valent metals have been prepared. The stannochlorides were obtained by crystallisation of acid solutions containing stannous chloride and the chloride of the second metal. To obtain the stannichlorides, these solutions were first subjected to the action of chlorine. The recorded analyses of the products, in which the water of crystallisation was obtained by difference, show that magnesium and zinc yield anhydrous stannochlorides, whilst those formed by potassium and ammonium contain two molecules of water of crystallisation. The data for the stannichlorides correspond with the following formulæ: $Li_2SnCl_6,8H_2O$; $Na_2SnCl_6,6H_2O$; K_2SnCl_6 ; Rb_2SnCl_6 ;
$$(NH_4)_2SnCl_6 ;$$
$CaSnCl_6$; $SrSnCl_6,4H_2O$; $MgSnCl_6,6H_2O$; $ZnSnCl_6,6H_2O$;
$CdSnCl_6$; $CoSnCl_6,6H_2O$; $NiSnCl_6,6H_2O$.

The anhydrous potassium, rubidium, and ammonium stannichlorides are quite stable in the air and do not deliquesce. The alkaline earth stannochlorides are entirely deliquescent, and on this account it was found impossible to obtain a pure specimen of the barium salt.

H. M. D.

Normal Zirconyl Nitrate. ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, **166**, 781—783).—The authors were unable to confirm the existence of a normal zirconium nitrate, $Zr(NO_3)_4,5H_2O$, commonly described in text-books. By evaporating a solution of zirconium hydroxide in nitric acid, even in an atmosphere saturated with nitric acid fumes, they always obtained a zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$, or at temperatures below $10°$ the *hydrate*, $ZrO(NO_3)_2,3\cdot5H_2O$. Attempts to prepare the anhydrous nitrate were not successful, the dehydration being always accompanied by loss of nitric acid.

W. G.

Basic Zirconyl Nitrates. ED. CHAUVENET and (MLLE.) L. NICOLLE (*Compt. rend.*, 1918, **166**, 821—824).—Zirconyl nitrate, $ZrO(NO_3)_2,2H_2O$ (compare preceding abstract), when dissolved in water, slowly undergoes hydrolysis, and there is slow formation of a precipitate having the composition $ZrO(NO_3)_2,ZrO_2,nH_2O$. A study of the neutralisation by $N/100$-sodium hydroxide of the nitric acid formed during the hydrolysis showed that there are two reactions, namely,

$$2ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO(NO_3)_2,ZrO_2 + H_2O$$
and $ZrO(NO_3)_2 + 2NaOH = 2NaNO_3 + ZrO_2 + H_2O$.
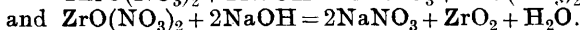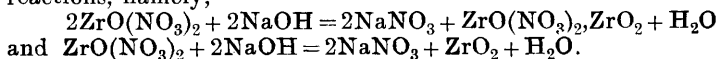
When the normal zirconyl nitrate is heated at 120° in the presence of nitric acid vapour, it undergoes dehydration, and at the same time loss of nitric acid, giving a *basic nitrate*, $3ZrO(NO_3)_2,ZrO_2,7H_2O$. If the dehydration takes place in air, there are formed the following basic nitrates: at 110°, $2ZrO(NO_3)_2,ZrO_2,7H_2O$; at 150°, $ZrO(NO_3)_2,2ZrO_2,4H_2O$; at 215°, $ZrO(NO_3)_2,7ZrO_2,5H_2O$; and at 250°, $ZrO(NO_3)_2,10ZrO_2,4H_2O$, and above this temperature zirconium oxide is formed. W. G.

The Resistance Limits of Mixed Crystals of Vanadium and Silicon with Iron. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 161—179; from *Chem. Zentr.*, 1918, i, 510).—The "resistance limit" is the term given to the composition of mixed crystals at which a sudden alteration occurs in the susceptibility to chemical agents. Whereas it is possible to observe in a direct manner the alterations in the surface of polished pieces of alloys consisting of copper–gold or silver–gold mixed crystals, this cannot be done in the present case, and it is necessary to observe, instead, the effect of various reagents on the metal. After ordinary, slow cooling, mixed crystals of iron and vanadium containing up to 0·43% molecule of the latter are ferromagnetic, whilst mixed crystals richer in vanadium are inactive. Examination was made of the behaviour of the mixed crystals towards solutions of various salts and acids, the resistance limit being found at $0·50 \pm 0·05$ mol. vanadium.

The iron–silicon mixed crystals gave rather irregular results; solutions of metallic nitrates cause the iron in the mixed crystals to become passive; the action of acids is also somewhat abnormal; copper sulphate, mercuric chloride, gold chloride, and several other salts, together with iodine, indicate a resistance limit at 0·25 mol. silicon, which appears to confirm the existence of the compound FeSi. D. F. T.

Mineralogical Chemistry.

The Old and the New Mineralogy. Sir HENRY ALEXANDER MIERS (T., 1918, **113**, 363—386).—A lecture delivered before the Chemical Society on April 18th, 1918. H. M. D.

Chemical Composition of Melanophlogites. E. MANZELLA (*Ann. Chim. Applicata*, 1918, **9**, 91—101. Compare Lasaulx, this Journal, 1876, ii, 54; Bertrand, A., 1881, 1000).—Melanophlogite, a mineral discovered by Lasaulx in association with certain specimens of sulphur, is characterised by its behaviour on heating, changing successively in colour to greyish-yellow, greyish-blue, and deep bluish-black. Purified specimens of various origin recently

examined had the following composition: hydrogen, 1·47 to 1·56; carbon, 3·32 to 3·91; silica, 88·76 to 89·12 sulphuric anhydride, 0·63 to 2·49; iron and loss, 0·27 to 0·60; and substances undetermined, 2·67 to 4·94%. A decrease in the proportion of sulphuric anhydride was accompanied by a reduction in the degree of blackening on heating, but other experiments showed that the alteration in colour must be attributed solely to carbonisation of the organic constituents in the mineral. C. A. M.

Analytical Chemistry.

Acidimetry of Coloured Solutions. An Application of the Pocket Spectroscope. ALFRED TINGLE (*J. Soc. Chem. Ind.*, 1918, **37**, 117; *J. Amer. Chem. Soc.*, 1918, **40**, 873—879).—A method is described whereby highly coloured acid solutions may be accurately titrated. The process depends on the fact that the absorption spectra of indicators are different in acid and in alkaline solutions. To make a determination, two similar vessels are taken, one of which contains the solution to be titrated and the other an equal volume of distilled water. To the latter, one drop of standard alkali is added, and then the indicator is slowly added from a burette until the characteristic absorption band shows a sufficiently sharp edge. The position of this edge is noted. Then the same volume of indicator is added to the solution to be estimated, and alkali added from a burette until the characteristic band is observed in the same position. This gives the end-point of the titration. The change does not involve the appearance of a new absorption band, but rather the shifting of a band already present. The method was tested on solutions of sulphuric acid of known concentration, which were coloured by the addition of neutral tea extract or liquorice. The results are quite as accurate as those obtained for colourless solutions by the ordinary method. The amount of indicator used is rather larger than that generally employed; the exact amount necessary must be found experimentally. In the present experiments, 1 c.c. of methyl-orange and 2·5 c.c. of cochineal extract were used.   J. F. S.

Mercuric Oxide as a Standard for Volumetric Analysis. L. ROSENTHALER (*Zeitsch. anal. Chem.*, 1918, **57**, 98).—Incze has recommended the use of yellow mercuric oxide as a standard in volumetric analysis (A., 1917, ii, 327), but the author points out that he and Abelmann had previously used mercuric oxide for the purpose (A., 1913, ii, 786).   W. P. S.

Detection of Anions. FRITZ FEIGL (*Zeitsch. anal. Chem*, 1918, **57**, 135—138).—The substance is boiled with concentrated sodium

carbonate solution or fused with a mixture of sodium and potassium carbonates; after filtration, the solution is nearly neutralised with nitric acid and warmed with the addition of an excess of solid zinc nitrate. The mixture is filtered; the precipitate contains zinc sulphide, sulphite, phosphate, borate, fluoride, ferrocyanide, ferricyanide, and cyanide, and also molybdate, vanadate, and tungstate, whilst the filtrate contains zinc thiocyanate, chloride, bromide, iodide, sulphate, thiosulphate, and sulphite. These substances are then identified by drop reactions without further separation [See also *J. Soc. Chem. Ind.*, July.] W. P. S.

Estimation of Chlorine in Organic Substances (Gastric Juice, Blood, Milk, etc.). SIROT and JORET (*Ann. Chim. anal.*, 1918, **23**, 109—113).—The total chlorine in gastric juice is estimated by Volhard's method after the sample has been treated with Esbach's reagent (10 grams of picric acid and 25 grams of acetic acid per litre of water) and filtered. Chlorine in organic and inorganic combination is estimated in the same way after the sample has been evaporated to expel free hydrochloric acid, whilst chlorine in inorganic combination is obtained by titrating the residue left after evaporation and incineration. In the case of blood, sodium metaphosphate is recommended as a clarifier; 20 c.c. of the blood are mixed with 75 c.c. of water, 10 drops of nitric acid, 20 c.c. of 5% sodium metaphosphate solution, and 1·5 c.c. of acetic acid. The mixture is then diluted to 200 c.c., filtered, and the chlorine titrated in the filtrate. The acetic acid–picric acid solution may be used for precipitating the casein, etc., in milk previous to the estimation of the chlorine present. W. P. S.

Gravimetric Analysis. V. [Chlorides, Bromides, and Iodides.] L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 101—103).—Chlorides, bromides, and iodides are precipitated by a small excess of N-silver nitrate in 100 c.c. of the cold solution to which has been added 5 c.c. of N-nitric acid, or, in presence of ferric salts, 10—20 c.c. In the case of chlorides and bromides, the mixture is left for one hour and then boiled; in the case of iodides, the silver is added first, the nitric acid after half an hour, and the mixture is boiled after another half-hour. Twenty-four hours later, the precipitate is collected on a plug of cotton wool in a Kelch funnel and dried at 132°. It is washed with 50 c.c. of water acidified with nitric acid, and later with 50 c.c. acidified with acetic acid. Correction values amounting to a few tenths of a mg., according to the weight of the precipitate, are used to improve the accuracy of the results. Iodides may also be precipitated in the presence of hydrochloric acid as palladium iodide. 0·5 Gram of palladium is dissolved in nitric acid and the solution evaporated to dryness several times with hydrochloric acid; the residue is taken up with 10 c.c. of 10% hydrochloric acid, 1 c.c. of alcohol is added to remove any free chlorine, and the solution made up to 100 c.c.. In absence of chlorides, the palladium iodide

remains in colloidal solution; when precipitated cold, it is floccu- lent, and becomes granular on heating. With a preponderating quantity of iodide, the neutral solution is diluted so that 100 c.c. will give about 0·1 gram of precipitate; 1·0 gram of sodium chloride is added, and 10 c.c. of palladium chloride solution, with agitation. The liquid is heated until the precipitate becomes granular, and the latter is collected on the cotton filter after twenty-four hours, washed with 100 c.c. of cold water, and dried at 132°. With small quantities of iodide, 100 c.c. of the liquid are acidified with hydro- chloric acid and precipitated with 1 c.c. of the palladium solution in the cold. The precipitate is allowed to remain for twenty-four or forty-eight hours, according to its quantity, and is collected in the flocculent condition. The palladium iodide is somewhat soluble in presence of alkali bromides; in presence of large quantities of chlorides, a small correction is applied.   J. F. B.

Titration Method for Chlorine, Bromine, Cyanogen, and Mercury. EMIL VOTOČEK (*Chem. Zeit.*, 1918, **42**, 257—260).— Chlorides may be titrated with standardised mercuric nitrate solu- tion in the presence of a small quantity of nitric acid; 0·06 gram of crystallised sodium nitroprusside is used as the indicator, and the volume of the solution should be about 250 c.c. Sulphates, phosphates, and chlorates do not interfere, but sulphites and nitrites must not be present. The method is trustworthy and more accurate than Volhard's method. [See further, *J. Soc. Chem. Ind.*, July.]
                                                                  W. P. S.

The Estimation and Distribution of Bromine in the Organs and in the Blood after Dosing with Sodium Bromide. W. AUTENRIETH (*Münch. med. Woch.*, 1918, **65**, 33—35; from *Chem. Zentr.*, 1918, i, 472—473).—Bromine in bromides of the alkali metals can be estimated colorimetrically by treating the acidified aqueous solution with potassium hydrogen sulphate and potassium permanganate, the liberated bromine being extracted with chloroform and the extract compared with a standard bromine solution, using the Autenrieth-Königsberger colorimeter. The method is not affected by the presence of chlorine and is especially suitable for small quantities. Organs such as liver, kidneys, brain, etc., are heated in a nickel crucible with pure sodium hydroxide and a little potassium nitrate, and the acidified solution treated in the manner described. Sodium bromide is retained tenaciously by the human organism, and only very slowly eliminated by the kidneys, its retention being favoured by a diet poor in chlorine. The brain shows no specific attraction for bromine.   D. F. T.

Gravimetric and Volumetric Estimation of Fluorine Precipitated as Thorium Fluoride. F. A. GOOCH and MATSUSUKE KOBAYASHI (*Amer. J. Sci.*, 1918, [iv], **45**, 370—376). —Investigation of the method described by Pisani (A., 1916, ii, 393)

showed that the acidity of the solution and the excess of pre-cipitant are important factors in the estimation of fluorine as thorium fluoride. The acidity of the solution (as free acetic acid) should be from $N/50$ to $N/5$, and the quantity of thorium added should not exceed by more than 50% the amount required for the precipitation. The thorium fluoride may be collected and ignited to oxide, the latter being taken as a measure of the thorium fluoride, $ThF_4,4H_2O$, or the excess of thorium, after filtration, may be pre-cipitated as oxalate and this titrated with permanganate solution (compare this vol., ii, 177). [See, further, *J. Soc. Chem. Ind.*, 391A.] W. P. S.

Time as a Factor in Gravimetric Analysis. I. Pre-cipitation of Sulphuric Acid. Z. KARAOGLANOW (*Zeitsch. anal. Chem.*, 1918, **57**, 77—98).—In the precipitation of sulphuric acid as barium sulphate, the rate at which the barium chloride solution is added has a considerable influence; the most trustworthy results are obtained when the addition is extended over a period of not less than 1·5 minutes. The concentration of the solutions, stirring, concentration of hydrochloric acid, etc., also have an influence, but temperature has little effect. The presence of potassium chloride decreases the amount of barium sulphate found, and to some extent counterbalances the effect of rapid precipitation, but this compensation depends on definite conditions of experiment.
W. P. S.

The Estimation of Sulphates in Urine. A. L. FLOHR (*Arch. Néerland. physiol.*, 1918, **2**, 346—351).—The benzidine method of Rosenheim and Drummond for estimating inorganic and ethereal sulphates gives satisfactory results. If the liquid becomes coloured after hydrolysis of the ethereal sulphates by hydrochloric acid, and the colour interferes with the titration, it can be removed sufficiently by treating the liquid with animal charcoal. S. B. S.

Estimation of Non-protein Nitrogen in Blood. ISIDOR GREENWALD (*J. Biol. Chem.*, 1918, **34**, 97—101).—A full account of work previously published (A., 1917, ii, 523). H. W. B.

New Method for the Direct Nesslerisation of Ammonia in Urine. JAMES B. SUMNER (*J. Biol. Chem.*, 1918, **34**, 37—41).—In the Folin and Denis direct Nesslerisation method (A., 1916, ii, 574), the Merck's blood charcoal may be replaced by copper sulphate. The urine is treated with a practically saturated solu-tion of copper sulphate (298 grams of the crystallised salt per litre). Copper hydroxide is then precipitated by adding a $2·03N$-sodium hydroxide solution until the neutral point is almost reached, when about 90% of the creatinine is also precipitated. The small amount of creatinine remaining in solution is not sufficient to interfere with the subsequent Nesslerisation.

For rough comparative tests, standard colours similar to those

obtained by Nesslerisation are prepared by dilution of a solution containing 6% of crystallised ferric chloride and 2·5% of crystallised cobalt nitrate.   H. W. B.

Apparatus for the Estimation of Nitric Acid by the Schulze-Tiemann Method. KARL LEUCHS (*Chem. Zeit.*, 1918, **42**, 235).—The decomposition flask is closed with a glass stopper provided with a tapped funnel and a delivery tube, and the stopper is surrounded by a water-seal. The delivery tube, which is bent downwards and under the lower end of the gas-collecting burette, is provided with a glass non-return valve. The whole apparatus is constructed of glass.   W. P. S.

Gasometric Estimation of Nitrates. C. A. HILL (*Analyst*, 1918, **43**, 215—216).—When an external reaction bottle is used in the estimation of nitrates by shaking the latter with sulphuric acid and mercury, it is necessary to fill the bottle previously with a gas inert towards nitric oxide. Carbon monoxide may be used for this purpose, and is prepared by heating a mixture of sodium formate and concentrated sulphuric acid. [See, further, *J. Soc. Chem. Ind.*, July.]   W. P. S.

New Volumetric Method for the Estimation of Phosphates in Urines. ARGEO ANGIOLANI (*Giorn. Farm. Chim.*, 1917, **66**, 251—252; from *Chem. Zentr.*, 1918, i, 571).—Twenty-five c.c. of the urine are treated with 1 c.c. of 20% hydrochloric acid, 1 gram of ammonium chloride, and 10 c.c. of a citric acid–magnesium solution (a solution of 35 grams of magnesium oxide in 260 grams of citric acid, the total bulk being 500 c.c., which is then treated with 400 c.c. of 10% ammonia solution and kept for two hours). The precipitate is collected, washed with very dilute ammonia solution, dried at 30—40°, and then dissolved in 50 c.c. of $N/10$-sulphuric acid, of which the excess is then titrated with $N/10$-sodium hydroxide solution, using methyl-orange as indicator. One c.c. of $N/10$-acid is equivalent to 3·55 mg. P_2O_5.   D. F. T.

Marsh's Apparatus. W. KIRKBY (*Pharm. J.*, 1918, **100**, 286).—A tube loosely packed with cotton wool is interposed between the generating flask and the hydrogen jet with the object of preventing any risk of explosion.   C. A. M.

Simple Process for the Estimation of Small Quantities of Arsenic in Corpses. H. FÜHNER (*Ber. Deut. Pharm. Ges.*, 1918, **28**, 221—229).—The process consists in the destruction of the animal matter by permanganate and sulphuric acid, the distillation of the solution with sodium chloride, and the estimation of the arsenic in the distillate by the Gutzeit method, using mercuric bromide paper. [See *J. Soc. Chem. Ind.*, July.]
                                                               J. H. J.

Estimation of Carbon Dioxide in Carbonates by Dittrich's Method. Béla von Horvath (*Chem. Zeit.*, 1918, **42**, 121).—Carbon dioxide may be estimated in sodium carbonate or barium carbonate by heating the same at dull redness with borax which has been heated previously at 1000°; the carbonate is decomposed readily, and the loss in weight gives the amount of carbon dioxide present. [See, further, *J. Soc. Chem. Ind.*, 369A.]

W. P. S.

Filtration of Silica. P. Nicolardot and J. Koenig (*Ann. Chim. anal.*, 1918, **23**, 104—109).—The fact that a minute quantity of silica passes into the filtrate when hydrated silica is evaporated to dryness and then collected on a filter does not appear to be due to solubility of the silica; the effect of successive evaporations and heating at 110° is to agglomerate the silica so that the whole of it is retained by a good filter. It is recommended that the silica be twice evaporated with hydrochloric acid and heated at 110°, but without intervening filtration, before it is collected; the filtrate may be passed once more through the filter. [See, further, *J. Soc. Chem. Ind.*, July.]

W. P. S.

Estimation of Strontium. L. W. Winkler (*Zeitsch. angew. Chem.*, 1918, **31**, i, 80 and 83—84).—*As Sulphate.*—One hundred c.c. of a neutral solution containing 0·5 gram of strontium salt are acidified with 1 c.c. of acetic acid, heated to the boiling point, and 10 c.c. of a 10% solution of sodium sulphate are added. Heating is continued until the precipitate is powdery, when it is left overnight. It is transferred to a Gooch crucible, washed with 50 c.c. of saturated strontium sulphate solution, and weighed after drying at 132°. If the filtrate is required further, alcohol is used as the washing agent. The presence of other salts, especially magnesium chloride and hydrochloric and nitric acids, leads to low results.

As Carbonate.—1·0 Gram of potassium nitrate and 10 c.c. of 10% sodium carbonate solution are added to a boiling solution of not more than 0·5 gram of strontium salt in 100 c.c. of solution. Next day the precipitate is washed with 50 c.c. of saturated strontium carbonate solution and weighed as $SrCO_3$ after drying at 132°. Owing to incomplete loss of carbon dioxide on ignition, the precipitate cannot be weighed as oxide.

As Oxalate.—The precipitation is made with 10% solution of potassium oxalate, and resembles that of the sulphate. After remaining overnight, the precipitate is washed with saturated strontium oxalate solution. It is dried at 100° for two hours and weighed as SrC_2O_4,H_2O, or at 132° for six hours and weighed as SrC_2O_4. Other salts, especially magnesium chloride, interfere. This is the most convenient and exact method of estimating strontium.

H. J. H.

Time as a Factor in Gravimetric Analysis. Precipitation of Barium Chloride with Sulphuric Acid. Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1918, **57**, 113—121).—In the gravi-

metric estimation of barium as barium sulphate, sulphuric acid should be used for the precipitation; alkali sulphates must not be used. The acid should be added rapidly; if it is added slowly, the results obtained are too low. [See, further, *J. Soc. Chem. Ind.*, 352a.]   W. P. S.

Volumetric Estimation of Lead by means of Ammonium Molybdate. LINDT (*Zeitsch. anal. Chem.*, 1918, **57**, 71—76).—In this process, it is essential that an excess of ammonium acetate should be avoided in dissolving the lead sulphate; the results obtained are too high in the presence of such excess, but are trustworthy when the lead sulphate is dissolved in the minimum requisite quantity of the acetate solution. [See, further, *J. Soc. Chem. Ind.*, 352a.]   W. P. S.

Estimation of Copper as Copper Oxide after previous Precipitation as Thiocyanate. G. FENNER and J. FORSCHMANN (*Chem. Zeit.*, 1918, **42**, 205—206).—The inconvenient drying of the cuprous thiocyanate precipitate to constant weight is unnecessary, and may be avoided by conversion of the precipitate into cupric oxide by roasting in a muffle at a temperature near 800°. [See also *J. Soc. Chem. Ind.*, 391a.]   D. F. T.

Analysis of White Metal. F. KUREK and A. FLATH (*Chem. Zeit.*, 1918, **42**, 133—134).—Tin is estimated by dissolving the alloy in hydrochloric acid with the addition of ferric chloride, reducing the tin with metallic iron, separating the precipitated antimony and copper, and titrating the filtrate with ferric chloride solution. The antimony and copper are then dissolved in hydrochloric acid to which potassium chlorate is added, excess of free chlorine is expelled by boiling the solution, the two metals are separated as their sulphides, the antimony sulphide is dissolved in sodium sulphide solution, again precipitated in the presence of an excess of oxalic acid, dissolved in hydrochloric acid, the solution boiled until the antimony is reduced, and then titrated with potassium bromate solution. Suitable methods are also described for the estimation of lead, copper, iron, aluminium, nickel, and zinc in the alloy. [See, further, *J. Soc. Chem. Ind.*, 877a.)
                                                                        W. P. S.

Use of Metallic Silver as a Reducing Agent in the Volumetric Estimation of Iron. GRAHAM EDGAR and A. R. KEMP (*J. Amer. Chem. Soc.*, 1918, **40**, 777—784).—The reaction between metallic silver and solutions of ferric sulphate in the presence of sulphuric acid and a soluble thiocyanate has been examined. The results obtained show that silver may be employed to effect the complete reduction of the ferric salt provided the dissolved silver is precipitated by thiocyanate. The resulting ferrous solution is filtered, treated with an excess of silver nitrate, and titrated with potassium permanganate. An alternative

method consists in titrating the excess of silver nitrate with standard thiocyanate.

The thiocyanate serves to show when the reduction is complete, and further advantages of the method are that silver is usually quite free from iron, that it does not reduce titanium at all, and that it reduces vanadium quantitatively to the quadrivalent condition. [Compare *J. Soc. Chem. Ind.*, 391A.] H. M. D.

Estimation of Iron in Lactic Acid. A. HARVEY (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 37—38).—Iron in lactic acid can be estimated very exactly by a colorimetric method in which the colour developed with potassium ferrocyanide is matched against the colour produced by standard iron solution. Potassium thiocyanate is useless F. C. T.

Quantitative Separation of Iron from the Cerite Metals in the presence of Calcium. A. WÖBER (*Zeitsch. landw. Versuchsw. Oesterr.*, 1917, **20**, 500—501; from *Chem. Zentr.*, 1918, i, 476).—A weighed sample is dissolved by prolonged treatment with 2% hydrochloric acid, and to an aliquot portion of the solution there is added tartaric acid in the proportion of approximately four grams to one of the substance. On saturating the solution with hydrogen sulphide and adding aqueous ammonia until a pure black precipitate of iron sulphide is obtained, the transiently precipitated hydroxides of the cerite metals are redissolved. The iron sulphide is treated in the usual manner, whilst the estimation of the cerite metals is effected by the method of Hauser and Wirth (A., 1908, ii, 778). D. F. T.

Estimation of Nickel with α-Benzildioxime. R. STREBINGER (*Chem. Zeit.*, 1918, **42**, 242—243).—The author agrees with Grossmann and Mannheim (A., 1917, ii, 391) that Atack's method of estimating nickel by precipitation with α-benzildioxime is trustworthy for small quantities of the metal. When, however, the quantity of nickel exceeds 0·025 gram, the precipitate contains a certain amount of occluded α-benzildioxime, and the results obtained are too high. In such cases, the precipitate should be ignited and the resulting nickel oxide weighed. W. P. S.

Estimation of Chromium in Chromium Salts, Chrome Liquors, Leather Ashes, and Chromium Residues. KARL SCHORLEMMER (*Collegium*, 1917, 345 and 371; from *Chem. Zentr.*, 1918, i, 377—378).—The solution of the chromium salt is treated cautiously with approximately N-sodium hydroxide until the precipitate has redissolved. Aqueous hydrogen peroxide of approximately 3% concentration is then added, and the solution is boiled until no more oxygen is liberated. The resulting solution is acidified with sulphuric acid, and the amount of chromate estimated by one of the usual volumetric methods. Leather ash or dry

chromium residues should be mixed with anhydrous sodium carbonate and magnesium oxide and roasted until yellow, the aqueous extract then being titrated after acidification. For the oxidation of solutions of very impure chromium salts, it is better to use alkaline potassium permanganate solution. The presence of iron in the ash of chrome leather may interfere with the chromium estimation.   D. F. T.

Estimation of Molybdenum. O. BINDER (*Chem. Zeit.*, 1918, **42**, 255).—When molybdenum is precipitated as sulphide and the latter then ignited to oxide, the oxidation is not complete unless the substance, after preliminary ignition, is treated with nitric acid, evaporated, dissolved in ammonia, reprecipitated with nitric acid, evaporated, and ignited. A correction must be made for any traces of matter which remain insoluble when the ignited oxide is dissolved in ammonia. [See, further, *J. Soc. Chem. Ind.*, July.]
                                                       W. P. S.

The Estimation of Molybdenum as Lead Molybdate. ROBERT STREBINGER (*Oesterr. Chem. Zeit.*, 1917, [ii], **20**, 226—228; from *Chem. Zentr.*, 1918, i, 378).—For the estimation of molybdenum in ferro-molybdenum, 0·5—1 gram is fused with 10 grams of sodium peroxide in an iron crucible. The product is extracted with 500 c.c. of water, and 100 c.c. are taken for the test; after the removal of any iron by the addition of nitric acid and then ammonia solution, the solution is neutralised with acetic acid, boiled, and treated successively with solutions of lead acetate (2—5 grams) with acetic acid (2 c.c.) in 30 c.c. of water, and ammonium acetate (10 grams) in 50 c.c. of water. After boiling for a short time, the precipitate is allowed to settle for six hours. The precipitate is removed by filtration, washed with dilute ammonium acetate solution, dissolved in diluted nitric acid, and reprecipitated by the addition of a solution of ammonium acetate (10 grams) in 50 c.c. of very dilute acetic acid. After twelve hours, the lead molybdate is again separated, washed, dried, and ignited at a moderate temperature before final weighing as $PbMoO_4$.   D. F. T.

A Colour Reaction of Thorium and Zirconium with Pyrogallolaldehyde. H. KASERER (*Chem. Zeit.*, 1918, **42**, 170).—On the addition of an aqueous solution of pyrogallolaldehyde to one of a thorium compound, a yellow colour is formed, and, after a time, a dirty yellow precipitate is produced, which when filtered off leaves a colourless filtrate. Zirconium compounds, after boiling or after the addition of hydrogen peroxide, give a similar colour and precipitate with cerium compounds; the yellow colour remains after boiling. In the presence of nitric, sulphuric, or hydrochloric acid, a colourless solution and no precipitate are produced. A solution containing only 0·1 mg. of thorium nitrate per 100 c.c. shows the colour clearly. Pyrogallol, pyrogallolcarboxylic acid, and protocatechualdehyde do not give this reaction.

The pyrogallolaldehyde is prepared by dissolving 38 grams of pyrogallol and 36·3 grams of formanilide in absolute ether, condensing this with 15·2 grams of phosphoryl chloride, and filtering after twelve hours. The residue is dissolved in alcohol and precipitated by sodium chloride. The crystals are treated with warm sodium hydroxide, a current of hydrogen is passed through the solution, after which it is acidified and the aldehyde extracted with ether and purified by conversion into the bisulphite compound.

A. B. S.

Graphic Methods of Analysis. Hans Gradenwitz (*Chem. Zeit.*, 1918, **42**, 221).—The composition of such mixtures as formaldehyde, methyl alcohol, and water, and ethyl acetate, alcohol, and water, may be found from the graphs given, the data to be determined being, in the first case, the specific gravity and the formaldehyde content, and in the second, the specific gravity and the ethyl acetate content. [See, further, *J. Soc. Chem. Ind.*, 392A.]

W. P. S.

Method for Detecting Small Quantities of Chloretone (Trichloro-*tert.*-butyl Alcohol) in Aqueous Solutions. T. B. Aldrich (*J. Biol. Chem.*, 1918, **34**, 263—267).—The solution containing the chloretone is subjected to steam distillation. If a large amount of chloretone is present, it crystallises in the cooler part of the condenser in needles. When only small amounts of chloretone are present, crystallisation may not occur, but if the distillate is placed in a small flask fitted with a reflux condenser and boiled for half an hour, needle crystals are then obtained in the condenser when the amount of chloretone exceeds 0·25 mg. If protein is present, it should be digested with pepsin and hydrochloric acid before the steam distillation is carried out. The presence of other organic solvents prevents the crystallisation, and thus interferes with the recognition of chloretone by this method.

H. W. B.

Estimation of Cholesterol in Blood. L. Kast, V. C. Myers, and Emma L. Wardell (*Proc. Soc. Exp. Biol. Med.*, 1917, **15**, 1—2; from *Physiol. Abstr.*, 1918, **3**, 31).—One c.c. of blood is extracted with chloroform, and in the extract the cholesterol is estimated colorimetrically by the Liebermann-Burchard reaction (compare *Physiol. Abstr.*, 1917, **2**, 675). The values obtained are lower than those of Bloor, but are believed to be more accurate.

W. G.

Cammidge's Method for the Estimation of [Reducing] Sugar in Urine. R. W. Garrow (*Pharm. J.*, 1918, **100**, 148—149).—In estimating sugar by this method (A., 1917, ii, 276), it is noticed in titrating back the excess of iodine with thiosulphate that up to the point where the blue starch iodide is discharged the solution is transparent, but immediately after the first end-point is reached a slight opalescence begins to appear, in-

creasing to a white precipitate of cuprous iodide, and the blue colour returns. The first discharge of the blue colour should be taken as the end-point, and the titration should be done as rapidly as possible. [See, further, *J. Soc. Chem. Ind.*, 276A.]

J. F. B.

Polarimetric Estimation of Dextrose in Urine. G. FRERICHS and E. MANNHEIM (*Apoth. Zeit.*, **33**, 34; from *Chem. Zentr.*, 1918, i, 380. Compare A., 1917, ii, 393).—A 100 c.c. flask containing 5 c.c. of lead acetate solution is filled to the mark with the urine and shaken well; the liquid is then filtered and examined in the polarimeter in a 2-dcm. tube, the rotation giving the content of anhydrous dextrose in grams per 100 c.c. of urine. The lead acetate solution should contain 10 grams of the salt and 5 grams of 30% acetic acid in 20 grams of water. If the lead acetate treatment fails to decolorise the urine sufficiently, the latter may be decolorised with charcoal, either at the same time as the lead acetate treatment or subsequently. As the charcoal absorbs a certain proportion of the dextrose, a correction becomes necessary, for which empirical values are given.   D. F. T.

Colorimetric Estimation of Dextrose in Urine. V. I. ISAACSON (*J. Lab. and Clin. Med.*, St. Louis, 1918, **3**, 289—294; from *Physiol. Abstr.*, 1918, **3**, 120).—A copper sulphate method, in which the unreduced copper is estimated after adding ammonia in a colorimeter against a standard.   S. B. S.

Estimation of Dextrose in Urine. C. H. HUGENHOLTZ (*Pharm. Weekblad*, 1918, **55**, 609—614).—A comparison of the iodometric, polarimetric, and fermentation methods of estimating dextrose in urine. The first method is very accurate, the second gives slightly low results, and the values derived from the third method are extremely erratic.   A. J. W.

Estimation of Sugar in Normal Urine. STANLEY R. BENEDICT and EMIL OSTERBERG (*J. Biol. Chem.*, 1918, **34**, 195—201).—In this method, which permits of the estimation of traces of sugar accurately to within a few thousandths of 1%, the creatinine and polyphenols, and most of the total nitrogen and the glycuronic acid, are first removed from the urine by precipitation with a mercuric nitrate reagent, and the dextrose then estimated colorimetrically after treatment with picric acid. The necessary special reagents are prepared as follows. Mercuric nitrate solution, by adding slowly 220 grams of mercuric oxide to 160 c.c. of concentrated nitric acid until it has dissolved, then boiling, cooling, and adding 60 c.c. of 5% sodium hydroxide solution. It is made up to 1 litre and filtered. Picrate–picric acid solution, by adding 36 grams of picric acid and 400 c.c. of hot water to 500 c.c. of 1% sodium hydroxide solution and shaking until the picric acid has dissolved. It is cooled and made up to 1 litre.

To perform the estimation, 15 or 20 c.c. of the urine are placed in a 500 c.c. beaker, together with an equal volume of the mercuric nitrate solution, and, after mixing, solid sodium hydrogen carbonate is added until frothing ceases and an alkaline reaction to litmus paper is obtained. After filtering, the excess of mercury is removed by adding a pinch of zinc dust and a drop or two of concentrated hydrochloric acid. From 1 to 4 c.c. of the final filtrate (containing about 1 mg. of dextrose) are measured into a large test-tube graduated to indicate 12·5 and 25 c.c. Water is added if required to bring the volume to 4 c.c., and 1 c.c. of 20% sodium carbonate solution is run in, followed by 4 c.c. of the picrate–picric acid solution. The mixture is heated in boiling water for ten minutes, cooled, diluted to the mark, and compared in a colorimeter with a standard solution similarly prepared from 1 mg. of dextrose in 4 c.c. of water or with a permanent standard of picramic acid or potassium dichromate solution. The former is prepared by adding 0·5 c.c. of 20% sodium carbonate solution and 15 c.c. of the picrate–picric acid solution to 105 c.c. of exactly 0·01% picramic acid solution in 0·02% sodium carbonate solution and then diluting to 300 c.c. with water. To prepare the dichromate standard, dissolve 0·536 gram of potassium dichromate in 1 litre of water.

To estimate the fermentable sugar, a second estimation in the urine after fermentation is necessary. About 20 mg. of dextrose and a one-quarter cake of yeast are added to 25 c.c. of the urine. After mixing, it is allowed to remain in an incubator at 35—38° for eighteen to twenty hours. The clear urine is then decanted and the estimation of dextrose carried out as above. The difference between the two estimations gives the fermentable sugar.

H. W. B.

Modification of the Lewis-Benedict Method for the Estimation of Dextrose in the Blood. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **34**, 203—207. Compare A., 1915, ii, 111). —The modification consists in adding the solution of picric acid in sodium picrate, employed in the estimation of dextrose in urine (see preceding abstract), instead of picric acid to the laked blood, which renders the subsequent evaporation unnecessary.

H. W. B.

Sources of Error in the Estimation of Dextrose by the Colorimetric Picrate Method. T. ADDIS and A. E. SHEVKY (*Proc. Soc. Exp. Biol. Med. New York*, 1918, **15**, 79).—The reddish-brown colour produced on heating dextrose, picric acid, and sodium carbonate varies with the temperature, duration of heating, and amount of carbonate present.

G. B.

Inversion and Estimation of Sucrose. A. R. ROSE (*Proc. Soc. Exp. Biol. Med. New York*, 1917, **15**, 16—17).— Heating for ten minutes at 100° with 2 volumes of saturated picric acid inverts the sucrose; then 1 vol. of 20% sodium carbonate

is added, and after a further twenty minutes' heating the total
dextrose + lævulose is estimated colorimetrically according to Lewis-
Benedict. The amount originally present is estimated in a similar
tube, in which the sodium carbonate was added before heating.
The difference between the two tubes represents invert-sugar (com-
pare preceding abstract).   G. B.

**Estimation of Furfuroids (Furfurosans) in the Different
Products of Beet Sugar Factories. I.** R. GILLET (*Bull.
Assoc. chim. Sucr. Dest.*, 1917, **35**, 53—62).—It is known that
other substances besides pentoses and pentosans yield more or less
furfuraldehyde under the well-known conditions of distillation with
hydrochloric acid. Chalmot has stated that sucrose yields not
more than 0·2%, but the author, operating on 5—20 grams of pure
sucrose, has obtained from 0·38 to 0·75%. of furfuraldehyde under
the Tollens-Councler conditions of working. The method of pro-
cedure is described fully, and attention is directed to certain points
which are of importance in securing uniform results. To prevent
superheating, the distillation flask should not be immersed in the
bath below the level of the liquid in the flask. The temperature
of the bath should be such as to produce uniform distillation at
the rate of 30 c.c. in twelve to fourteen minutes; when operating
on 10 grams of sucrose, the author found it necessary to heat the
bath to 155—160°, since at lower temperatures distillation was
slow and the distillate was often cloudy, owing to the presence of
an unknown, yellow substance in suspension. Great importance is
attached to strict adherence to the prescribed method of replenish-
ing the acid during distillation, exactly 30 c.c. being added as soon
as 30 c.c. has distilled. In spite of attention to these and other
details of procedure, it was found impossible to secure absolutely
uniform yields of furfuraldehyde from sucrose.   J. H. L.

**Colour Reaction for Ground Wood Pulp or the Incrusting
Matters of Wood with Phenylhydrazine Hydrochloride.**
S. JENTSCH (*Zeitsch. angew. Chem.*, 1918, **31**, 72).—An aqueous
solution of phenylhydrazine hydrochloride gives an intense orange-
yellow coloration with raw wood fibre, which subsequently changes
to a characteristic bright green on drying in presence of air; the
appearance of the green colour is accelerated by suitable heating.
Cotton and other pure cellulose fibres are stained only to a pale
yellow, which changes to a characteristic light brown after drying.
The above test for lignocellulose is stated to be sharper and more
definite than the phloroglucinol–hydrochloric acid test. [See also
J. Soc. Chem. Ind., 365A.]   J. F. B.

New Reaction of Formic Acid and Hyposulphites.   E.
COMANDUCCI (*Boll. chim. farm.*, 1918, **57**, 101—102).—The
presence of formic acid in a liquid may be detected by heating the
latter gently with concentrated sodium hydrogen sulphite solution
until gas bubbles begin to escape, the liquid being then cooled and

fresh, dilute sodium nitroprusside solution poured carefully on to its surface; a green or blue ring is thus formed, hydrogen cyanide being liberated at the same time. The blue precipitate, $Na_4Fe_2(CN)_9$, results from the interaction of the nitroprusside and sodium hyposulphite, the latter being formed by the action of the formic acid on the sodium hydrogen sulphite (compare A., 1904, ii, 845). **T. H. P.**

Estimation of Lactic Anhydrides in Lactic Acid. F. C. THOMPSON and KYOHEI SUZUKI (*J. Soc. Leather Trades' Chem.*, 1918, **2**, 115—121).—Lactide reacts completely in the cold with alkali hydroxide in ten minutes if the alkali is in considerable excess. No heating is therefore necessary in the analysis of lactic acid. Furthermore, the proportion of lactide present in lactic acid depends on the dilution and time of keeping, so that analytical results do not indicate the amount of lactide in a dilute solution used in technical practice, for example, in deliming hides. [See, further, *J. Soc. Chem. Ind.*, 343A.], **F. C. T.**

An Optical Method for the Estimation of Malic and Tartaric Acids in the same Solutions. J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 693—704).—The method depends on the facts that uranyl acetate enhances the rotation of *l*-malic and *d*-tartaric acids, whilst ammonium heptamolybdate reverses the direction of the rotation in the case of *l*-malic acid, giving strongly positive solutions in each case. A chart is made connecting the rotations of solutions, containing up to 1% of the acids, activated by uranyl acetate on the one hand (the curves slope down from left to right) with those of solutions activated by ammonium heptamolybdate on the other (the curves slope up from left to right). The point of intersection of a given pair of curves will give, therefore, the number of grams of tartaric acid on the abscissæ and the proportion of malic acid on the ordinates.

The details of the method are based on Yoder's work on malic acid (A., 1911, ii, 1141) and further developments by Gore and others in America, which have been embodied in an official process (*J. Assoc. Off. Agric. Chemists*, 1916). An amount of the sample is taken which, judged by titration, will contain at least about 0·1 gram of either acid and not more than 0·6 gram of tartaric acid or 0·8 gram of malic acid. This is neutralised with *N*-ammonia solution, mixed with 2 vols. of 95% alcohol, filtered from pectins, and the filtrate slowly mixed with an excess of a 10% solution of barium chloride in 50% alcohol, and then made up to fourteen times the original volume with 95% alcohol. The precipitate is collected by centrifuging, boiled with water, mixed with 10 c.c. of 20% ammonium sulphate solution, the mixture is concentrated to about 80 c.c., cooled, mixed with 6 c.c. of glacial acetic acid, and·diluted to 100 c.c. Two 25 c.c. portions of the clear solution, after centrifuging, are taken, mixed with 10 c.c. of an 8% solution of pure uranyl acetate and 10 c.c. of 10%

ammonium heptamolybdate respectively, left for three hours in the dark, and then polarised at about 20° in a 2-dcm. tube. If the molybdate solution becomes green through reduction, a drop of bromine water may be added.   J. C. W.

Estimation of Fatty Acids in Butter Fat.   E. B. HOLLAND and J. P. BUCKLEY, JUN. (*J. Agric. Research*, 1918, **12**, 719—732). —Direct esterification of butter fact (with absolute alcohol containing hydrogen chloride or concentrated sulphuric acid). and subsequent fractional distillation of the resulting esters, affords a trustworthy method for the estimation of certain of the fatty acids. The following quantities of fatty acids were found in butter fat: hexoic acid, 1·36%; octoic acid, 0·975%; decoic acid, 1·831%; lauric acid, 6·895%; myristic acid, 22·618%. Butyric acid (3·153%) and palmitic acid (19·229%) were estimated by difference, stearic acid (11·384%) by crystallisation, and oleic acid (27·374%) from the iodine number of the insoluble fatty acids. [See, further, *J. Soc. Chem. Ind.*, 846A.]   W. P. S.

Test for Acetone in Urine.   M. WAGENAAR (*Pharm. Weekblad*, 1918, **55**, 57—60).—The presence of 0·5 mg. of acetone in 10 c.c. of urine can be detected by mixing the sample with a solution of acetic acid, tartaric acid, and sodium nitroprusside, and covering the liquid with a concentrated solution of ammonia. A coloration like that of permanganate solution is developed at the junction of the liquids.   A. J. W.

Detection of Acetone in Urine.   P. BOHRISCH (*Pharm. Zeit.*, 1918, **63**, 173—174. Compare this vol., ii, 179).—The author finds that Legal's test is more sensitive than Lange's ring test, and mentions that Arends and Urban had shown in 1911 that it was not necessary for the sodium nitroprusside solution used in the tests to be freshly prepared.   W. P. S.

Detection of Arbutin.   HANS SALOMON (*Ber. Deut. pharm. Ges.*, 1918, **28**, 138—139).—The tests commonly applied for arbutin in urine, for example, after the ingestion of bearberry leaf tea, are not specific to this substance.   D. F. T.

Direct Estimation of Urea and Ammonia in Placenta Tissue.   FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1918, **33**, 381—385. Compare Sumner, A., 1916, ii, 655).—The methods of estimation recommended by the author are essentially those devised by Sumner (*loc. cit.*), the chief modification being the addition of potassium carbonate in a solid form to liberate the ammonia prior to aeration.   H. W. B.

Estimation of Uric Acid in Urine and Blood.   D. G. COHEN TERVAERT (*Arch. Neerland. physiol.*, 1918, **2**, 337—345).—In the case of urine, the uric acid is precipitated by ammonium chloride as ammonium urate under conditions described by the author in detail. The precipitate is washed with ammonium chloride by

centrifugalisation, then dissolved in lithium carbonate solution, and the uric acid is estimated colorimetrically by Folin's phosphotungstate reagent in a solution made alkaline by sodium carbonate. In the case of blood, the proteins are separated by coagulation of the solution acidified by acetic acid, the filtrate is concentrated to a small bulk, and the uric acid is precipitated as urate and the amount estimated in a manner similar to that described for the estimation of uric acid in urine.   S. B. S.

Estimation of Uric Acid in the Blood by Titration with Permanganate. J. LUCIEN MORRIS (*Proc. Amer. Soc. Biol. Chem.*, 1917, xxi; *J. Biol. Chem.*, 1918, **33**. Compare A., 1917, ii, 279).—The uric acid from 20 c.c. of blood is isolated as zinc urate. It is then dissolved in hydrochloric acid and disodium hydrogen phosphate added until all the zinc is reprecipitated. A saturated solution of sodium hydrogen carbonate (25 c.c.), 10% potassium iodide (5 c.c.), and 0·5% starch solution (1 c.c.) are added, and 0·002N-permanganate run in from a burette until the blue colour of iodide of starch appears. In the slightly alkaline solution, the oxidation of the potassium iodide, and consequent production of the blue iodide of starch, does not occur until all the uric acid has been oxidised. The results are accurate to within 5%.   H. W. B.

Homatropine and the Vitali Test. H. DROOP RICHMOND (*Analyst*, 1918, **43**, 167—168).—Although the Vitali test serves to distinguish homatropine or its hydrobromide from atropine, hyoscyamine, or hyoscine, it is untrustworthy when applied to homatropine sulphate, since the sulphuric acid in this salt causes the production of a violet coloration. In testing the sulphate, the alkaloid should be isolated and the reaction applied to it instead of to the original salt.   W. P. S.

Microchemical Tests for Choline. N. SCHOORL (*Pharm. Weekblad*, 1918, **55**, 363—369).—A description of the microchemical characteristics of double salts of choline hydrochloride with platinum chloride, gold chloride, mercuric iodide, bismuth iodide, and of the picrate and picrolonate.   A. J. W.

Estimation of Creatinine and of Creatine in the Blood. ISIDOR GREENWALD and GRACE MCGUIRE (*J. Biol. Chem.*, 1918, **34**, 103—118).—The new method consists in removing the blood-proteins by heat coagulation in dilute acetic acid solution, and then shaking with kaolin, which almost completely removes the creatinine, leaving the creatine unaffected. After filtration and concentration, the creatine is hydrolysed by hydrochloric acid and estimated by Folin's colorimetric method.   H. W. B.

Detection and Estimation of Quinine in Blood and Urine. W. RAMSDEN and I. J. LIPKIN (*Ann. Trop. Med. Parasitol*, 1918, **11**, 443—464).—The thalleioquinine reaction is rendered more delicate

(1 : 40,000 with certainty) by adding to 10 c.c. of the quinine solution, feebly acidified with hydrochloric acid and shaken in a test-tube, one-tenth saturated bromine water drop by drop until the pale yellow colour is no longer instantly discharged (white background). At intervals of five seconds, lots of about 2 c.c. are poured into test-tubes containing one drop of concentrated ammonia. Finally, all ammonia solutions are mixed, and the green pigment is extracted with chloroform. The Herapath test may, with Christensen's reagent and a polarising microscope, be employed for the recognition of 1/500 mg. of quinine. Mayer's reaction (ordinarily 1 : 500,000) may be rendered twenty times as delicate by extracting the alkaloid with ether free from all traces of aldehyde or acetone, dissolving in saturated ammonium sulphate solution, and adding 1/100 volume of the reagent. Potassium triiodide (limit, 1 : 1,500,000) is less suitable, on account of the colour; phosphotungstic acid and bismuth potassium iodide are much less delicate.

Blood is boiled with ammonium sulphate, urine is precipitated with lead acetate and ammonium sulphate in the presence of acetic acid; in either case, after. addition of ammonia to the filtrate, the quinine is extracted with ether free from ketones, the ether is evaporated, and the residue is dissolved in saturated ammonium sulphate solution (at least 10 c.c. for each mg. of quinine). The turbidity due to Mayer's reagent is compared nephelometrically with that in saturated ammonium sulphate solutions containing known amounts of quinine (gauged test-tubes in box with slit for illumination, dark-room, best dilution of quinine 200—300 c.c. per mg.). Thus 0.02—0.03 mg. of quinine in 5 c.c. of blood may be estimated with an error of less than 5%. Larger quantities of quinine (100 mg.) may be precipitated as periodide, from which the quinine is recovered with sodium hydrogen bisulphite and ether, so that it may be weighed or titrated. Gordin's volumetric method (A., 1900, ii, 114, 777; 1907, ii, 487; 1902, ii, 186) is found to be accurate. G. B.

Detection of Proteins by Bleaching Powder and Hydrochloric Acid. ADOLF JOLLES (*Deut. med. Woch.*, **43**, 1620—1621; from *Chem. Zentr.*, 1918, i, 303—304).—The test mentioned in the title is not sufficiently sensitive, and can be replaced by the following "three-tube test." The specific reagent contains 10 grams of mercuric chloride, 20 grams of citric acid, and 20 grams of sodium chloride in 500 c.c. of water. To three tubes are added 5 c.c. of filtered urine, to the first tube 1 c.c. of 30% acetic acid + 5 c.c. of the reagent; to the second, 1 c.c. of acetic acid + water, and to the third, water only. All tubes are made to contain the same volume of liquid. By comparing differences in the turbidities after remaining for ten minutes, it is possible to ascertain whether traces of proteins are present. S. B. S.

General and Physical Chemistry.

Optics of Disperse Systems. II. I. LIFSCHITZ and JENS BRANDT (*Kolloid Zeitsch.*, 1918, **22**, 133—143. Compare this vol., ii, 181).—The refractive power of disperse systems has been examined by observations on colloidal solutions of sulphur and on soap solutions.

The results obtained with colloidal solutions of sulphur, fractionated by the method described by Odén, show that the refractive index increases with the concentration of the solution (grams per 100 c.c.) according to a linear equation. The density of the sols also increases with the concentration in an approximately linear manner. The value of $(d_s - d_0)/c$, in which d_s is the density of a sol of concentration c and d_0 the density of the solvent, is, however, much greater than for solutions of sulphur in carbon disulphide in which the sulphur is present in the molecular condition. The refractivity, measured by Gladstone and Dale's formula, is much more nearly constant than it is when the formula of Lorenz and Lorentz is employed.

The results obtained in measurements of the refractive index of aqueous solutions of sodium oleate, palmitate and stearate, and of potassium palmitate at 70° show that the refractive index changes with the concentration according to a linear formula. The molecular refractivities of the soaps appear to be independent of the concentration, and consequently of the degree of dispersity and of the extent to which the soaps are hydrolysed and dissociated.

H. M. D.

Effect of an Electric Field on the Spectrum Lines of Helium. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 325—334).—The mode of resolution of the lines λ 5048, λ 5016, λ 4922, λ 4472, λ 4438, λ 4388, and λ 4121 under the influence of electric fields varying in intensity between 3000 and 70,000 volts per cm. is described. With the exception of λ 4686, the resolution of all the helium lines examined has been found to be unsymmetrical with respect to the initial line.

H. M. D.

Effect of an Electric Field on the Spectrum Lines of Hydrogen. II. TOSHIO TAKAMINE and USABURO YOSHIDA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 321—323. Compare A., 1917, ii, 402). —The changes produced by the action of a strong electric field have been examined by the investigation of a further series of hydrogen lines. The photographs show that the outer components of the lines belonging to the Balmer series frequently extend into the region of the unaffected secondary lines. The apparent lack

of any connexion between the two groups of lines suggests that they are due to different carriers. H. M. D.

Effect of an Electric Field on the Spectrum Lines of Hydrogen.

SHIGEHARU NITTA (*Mem. Coll. Sci. Kyoto*, 1917, **2**, 349—355. Compare preceding abstract).—The Stark effect has been examined with electric fields of considerably greater intensity than those used by previous observers. The H_β line yields six components, the separation of which is proportional to the intensity of the field. In addition to the Balmer lines, certain lines belonging to the secondary spectrum were investigated. H. M. D.

Optical Investigations on the Constitution of the Nitrates.

KONR. SCHAEFER (*Zeitsch. wiss. Photochem.*, 1918, **17**, 193—217. Compare A., 1910, ii, 562; 1917, ii, 61, 186).—The ultra-violet absorption of aqueous solutions of various nitrates has been examined over a considerable range of concentration. The results obtained for glucinum, silver, thallous, copper, mercurous, cerous, bismuth, and thorium nitrate are shown in the form of logarithmic absorption curves. On examining the available data for the nitrates, it would seem that these may be divided into three groups according to their optical behaviour at different concentrations. The nitrates of the alkali and alkaline earth metals satisfy the requirements of Beer's law. This relation is only approximately satisfied by the nitrates of glucinum, magnesium, aluminium, manganese, zinc, cadmium, lead, cobalt, and nickel, which form the second group. The deviations are partly due to hydrolysis and in part to the superposed absorption effect of the metal. To the third group belong the nitrates of metals which show large divergences from Beer's law. The absorption of the nitrates in this group (copper, silver, thallous, mercurous) increases rapidly with increase in the concentration of the solutions. This grouping of the metallic nitrates shows an undoubted connexion between the optical properties and the electro-affinity of the metals. The nitrates of the strongly electropositive metals show the selective absorption which has been attributed to that arrangement of the atoms which is found in the nitrate ion, as distinguished from the non-selective absorption of the grouping which is characteristic of the organic nitrates and of concentrated nitric acid. The absorption exhibited by the nitrates of the weak electropositive metals cannot be satisfactorily explained in terms of these two forms of the nitrate group, and it is suggested that the optical behaviour affords evidence of a third configuration of the atoms in the nitrate group.

The absorption of fused potassium nitrate has also been examined, and the selective absorption which it exhibits resembles closely that found for aqueous solutions of the alkali nitrates. In this respect it differs markedly from the absorption of anhydrous nitric acid, which shows no selective effect, although this is shown by dilute aqueous solutions of the acid. H. M. D.

Spectral Reaction of Methylfurfuraldehyde and β-Hydroxy-δ-methylfurfuraldehyde. (KINTARŌ OSHIMA and TETSUTARŌ TADOKORO (*J. Tokyo Chem. Soc.*, 1918, **39**, 23—30. Compare Oshima and Tollens, A., 1901, ii, 484).—A comparison of the absorption spectrum of samples of hydroxymethylfurfuraldehyde (as phloroglucide in hydrochloric acid solution) from various sources shows identity of the substance prepared by Kiermayer's method with that obtained from dextrose, lævulose, or inulin by distillation with hydrochloric acid. With hydroxymethylfurfuraldehyde prepared from galactose and lactose, the absorption band is shifted a little towards the F-line, and even slightly overlaps that line in the case of samples prepared from sucrose. These different absorption spectra can, however, be readily distinguished from that given by methylfurfuraldehyde. S. H.

The Relationship between the Optical Rotatory Powers and the Relative Configurations of Optically Active Compounds. The Influence of certain Inorganic Haloids on the Optical Rotatory Powers of α-Hydroxy-acids, α-Amino-acids, and their Derivatives. GEORGE WILLIAM CLOUGH (T., 1918, **113**, 526—554).—The author has compared the effect of sodium haloid salts on the optical rotatory powers of *l*-lactic, *d*-glyceric, *l*-malic, and *d*-tartaric acids and certain of their esters, and the effect of introducing a given radicle into the molecules of the configuratively similar hydroxy-acids, *l*-lactic, *l*-glyceric, *d*-malic, and *d*-tartaric acids, and from his results assumes that the optical rotatory powers of similarly constituted compounds possessing the same configuration are in general influenced similarly by the same changes in the external conditions and also by the introduction of the same substituent into a given radicle attached to the asymmetric carbon atom. The rotatory powers of the above four acids and of *d*-α-hydroxybutyric, *l*-α-hydroxy*iso*valeric, *d*-α-hydroxy*iso*hexoic, *d*-α-hydroxy-β-phenylpropionic, and *d*-α-hydroxyglutaric acids and their derivatives indicate that all these acids possess the same relative configurations, and they are designed as "*d*"-acids. Of the naturally occurring α-amino-acids, it is similarly assumed that *d*-alanine, *l*-serine, *l*-aspartic acid, *d*-valine, *l*-leucine, *d-iso*leucine, *d*-α-aminobutyric acid, *d*-glutamic acid, *l*-phenylalanine, and *l*-tyrosine all possess the same configurations, denoted by the symbol "*l*." The dextrorotatory (*d*-) α-halogen acids which have been isolated are assumed to be configuratively similar compounds and related configuratively to the "*l*"-amino-acids, which it is suggested are enantiomorphously related to the "*d*"-hydroxy-acids. This is supported by a comparison of the rotatory powers of the optically active α-bromoacylamino-acids with those of the α-aminoacylamino-acids. W. G.

The Radioactivity of the Waters of Neuchâtel and Seeland. H. PERRET and A. JAQUEROD (*Arch. Sci. phys. nat.*, 1918, [iv], **45**, 277—297, 336—348, 418—437).—The content in

radium emanation of the spring waters in a very small region, the
Neuchâtel Jura mountains and neighbourhood, has been ex-
haustively studied. Then a minute parallel study of two regions,
each of only a few square kilometres, and, lastly, the prolonged
parallel study of two springs in the same district and then in
different districts, were carried out. More than a hundred springs
were examined. The radioactivity of these springs is feeble and
varies between 0 and 3.5×10^{-10} curie of emanation per litre, the
quantity varying in all the springs considerably with the time.
No relation was found between radioactivity and the volume of
flow of the spring or its temperature, and the few thermal and
mineral springs found were not especially radioactive. In passing
across the Jura chain from S.E. to N.W., there is a marked increase
in the radioactivity of the water. The crystalline rocks beneath
come nearer to the surface in travelling in this direction. The
two springs examined continuously showed maxima and minima
of radioactivity recurring at the same intervals of time. The
quantity of radioactive salts in the waters was too small to be
detected.   F. S.

Sign of the Zinc Electrode. WILDER D. BANCROFT (*J.
Physical Chem.*, 1918, **22**, 371—379).—A theoretical paper in
which the sign given to potential values is discussed. It is pointed
out that with electrodes which form cations, the $E.M.F.$ is a
measure of the difference of the chemical potentials, but has the
opposite sign; with electrodes which form anions, the two potentials
have the same sign. Since the electrical potential of the copper
in a Daniell cell is higher than that of the zinc, and since the zinc
electrode is the place of lowest electrical potential, although highest
chemical potential, it follows that the minus sign ought to be used
when writing the potential difference $Zn \mid ZnSO_4$. This is in keep-
ing with the practice of physicists and physical chemists.
                                                          J. F. S.

**Photochemical Cell, containing Complex Cyanides of
Nickel or Platinum.** SATOYASU IIMORI (*J. Tokyo Chem. Soc.*,
1918, **39**, 1—13).—A photochemical cell was constructed with
platinum electrodes, which were immersed in a solution of potassium
nickel cyanide or potassium platinocyanide, one only of the elec-
trodes being exposed to light. In this cell the electrode exposed to
light is positive, but in a photochemical cell containing a solution
of potassium ferrocyanide, previously described by the author (*ibid.*,
1917, **38**, 507), it was negative. The current from the present cell
decays rapidly when the circuit is closed, notwithstanding the
insertion of a considerable resistance, but in the former cell a
constant current was obtained during the exposure to light. The
cause of the $E.M.F.$ of this cell is not yet known with certainty,
but it would seem not to be the photoelectrical effect on the elec-
trode, as it is not observed when the complex cyanides are replaced
by other salt solutions.   S. H.

Method for Determining the Temperature of Luminous Flames. HERMANN SENFTLEBEN and ELISABETH BENEDICT (*Physikal. Zeitsch.*, 1918, **19**, 180—181).—The temperature of luminous flames is obtained by inserting thin platinum or gold wires into the flame and estimating the temperature of the wires by means of a Holborn-Kurlbaum pyrometer. To compensate for the loss of temperature occasioned by the insertion of the wire, it is raised to the temperature of the flame by the passage of an electric current. When the wire and flame are exactly at the same temperature there is no deposition of carbon, but if the temperature of the wire is lowered slightly there is an immediate deposition of carbon. To correct, if necessary, for the change of temperature brought about by change in the shape of the flame owing to the insertion of the wire, measurements were made with wire of varying diameters (0·2—1·0 mm.), and it was shown that only at greater diameters than these does the temperature depend on the thickness of the wire. The temperature of the middle of a Hefner lamp flame determined by this method is found to be 1690° abs., which is about the mean of the previously recorded values (1680—1711°). J. F. S.

Improved Form of Thermo-regulator. JOHN B. FERGUSON (*J. Amer. Chem. Soc.*, 1918, **40**, 929—930).—The adjustment of the level of the mercury in the regulator tube is made by means of a plunger, and the mercury makes contact with a fixed platinum wire. H. M. D.

Thermo-regulator for Apparatus fitted with a Constant Water-level. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1918, **57**, 162—164).—The overflow water from the apparatus is conducted into one limb of a U-tube, the lower part of which is constricted and filled with mercury; the excess of water leaves the upper end of the limb of the U-tube through a side tube, a small by-pass being also fitted at the lower part of the limb. The other limb contains a floating valve, the lower end of which rests on the surface of the mercury. Should the supply of water be interrupted, the limb of the U-tube empties through the by-pass, decreasing the pressure on the mercury, and the valve falls, thus cutting off the supply of gas to the burner under the apparatus. W. P. S.

Cineole as a Solvent in Cryoscopy. CHARLES E. FAWSITT and CHRISTAIN H. FISCHER (*J. Roy. Soc. New South Wales*, 1918, **51**, 467—472).—Cineole is an oil of the formula $C_{10}H_{18}O$ which occurs largely in oil of eucalyptus. It is extracted by simple freezing. This substance has b. p. 175—176°. m. p. 0·9°, it is very hygroscopic, and the presence of water in the product accounts for the m. p. −1° usually given. Cineole is not generally useful as a cryoscopic solvent, chiefly on account of its hygroscopic properties, but in some cases it is found to be a more suitable solvent than benzene, although somewhat more difficult to work with. It has a cryoscopic constant 6·7 and a latent heat of fusion 22·2 cal. per gram. J. F. S.

The Saturated Vapour Processes of Penta-atomic Substances. E. ARIÈS (*Compt. rend.*, 1918, **166**, 935—939).—Taking Young's values for the physical constants of stannic chloride, the author deduces the formula $\Pi = \tau^{20/7}Z/x$, where

$$x = \{1 + (1 - \tau)(0\cdot84 - \tau)/[1\cdot8(1 - \tau)^2 + 0\cdot9]\}\tau^{13/7}$$

for the saturated vapour pressures of penta-atomic substances. The values calculated from this formula for methyl fluoride are in fairly close accord with those observed by Collie, except at a temperature of $-5°$. There is not such close agreement in the case of chloroform with the values as obtained by Regnault unless the critical constants of chloroform are taken as $247°$ and $45\cdot26$ atmos.   W. G.

Rapid Pressure Method for the Determination of Molecular Weights and Hydrogen Equivalents. W. H. CHAPIN (*J. Physical Chem.*, 1918, **22**, 337—344).—A modification of the vapour density method of determining molecular weights by measuring the pressure set up by a known weight of vapour in a known volume at a measured temperature. The apparatus used consists of a 500 c.c. distilling flask the side tube of which is replaced by a mercury manometer. The manometer tube is 5 mm. diameter and 20 cm. high, and is fitted with a sliding celluloid scale. The top of the flask is fitted with the usual device for dropping in the substance at the right moment. The method is available for all liquids boiling below $90°$. The substance is volatilised by steam, and as the whole of the apparatus is not at a uniform temperature, the average temperature must be computed. A method for deducing the average temperature is indicated. The usual precautions are taken in making the pressure measurement. An interesting innovation is introduced in the use of gelatin capsules for weighing the substance under investigation.

The same apparatus can be used for the determination of the equivalents of the metals zinc, aluminium, sodium, calcium, and magnesium. In all cases except sodium, weighed quantities of the metals are dropped into a measured volume of N—$3N$-hydrochloric acid contained in the bulb of the apparatus; with sodium, alcohol is used.   J. F. S.

Heat of Formation of the Anhydrous Calcium Borates. R. GRIVEAU (*Compt. rend.*, 1918, **166**, 993—995).—The pure anhydrous calcium borates were prepared by adding the calculated quantity of calcium carbonate to fused boric anhydride. The heat of solution of each of these borates in $N/2$-hydrochloric acid was then determined, and from these results the heat of formation of each borate was calculated, the results obtained being given by the equation :

$2B_2O_3$ sol. $+ CaO$ sol. $= 2B_2O_3,CaO$ sol. $+ 39\cdot8$ cal.

B_2O_3 sol. $+ CaO$ sol. $= B_2O_3,CaO$ sol. $+ 30\cdot9$ cal.

B_2O_3 sol. $+ 2CaO$ sol. $= B_2O_3,2CaO$ sol. $+ 48\cdot5$ cal.

B_2O_3 sol. $+ 3CaO$ sol. $= B_2O_3,3CaO$ sol. $+ 62\cdot2$ cal.
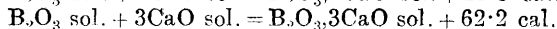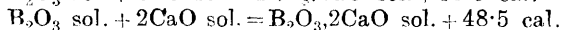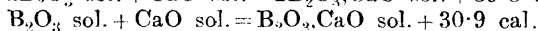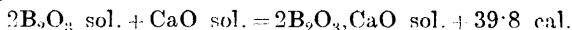
The energy of combination of each successive molecule of calcium oxide with two molecules of boric anhydride diminishes from 39·8 cal. to 13·7 cal.   W. G.

Apparatus for Cleansing Pyknometers. MARCEL DUGARDIN (*Ann. Chim. anal.*, 1918, **23**, 125—126).—A narrow glass tube, connected with a flask and a water-pump, is passed down the neck of the pyknometer so that the contents of the latter may be drawn off; water is then admitted to the pyknometer and drawn off again by means of the narrow tube.   W. P. S.

Adsorption Compounds. R. HALLER (*Kolloid Zeitsch.*, 1918, **22**, 113—133).—The formation of adsorption compounds by the interaction of dyes with other substances has been examined. Towards chemically indifferent solvents, adsorption compounds behave like mechanical mixtures. Adsorption compounds with a colourless adsorbent when dissolved in a suitable solvent show the same absorption spectrum as the corresponding solution of the dye. The melting points of adsorption compounds containing an adsorbent of low melting point are not very different from the melting point of the adsorbent. The general physical behaviour of the so-called adsorption compounds leads, therefore, to the conclusion that these are to be regarded as mechanical mixtures. [Compare *J. Soc. Chem. Ind.*, 411A.]   H. M. D.

Certain Relations between Crystalline Form, Chemical Constitution, and Optical Properties in Organic Compounds. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 277—285, 319—327).—In the expectation that there should be discoverable some relationship between the optical and the geometrical constants of crystals, an investigation has been made of a number of organic substances typical of the different classes of the tetragonal system. Making use of the Lorentz-Lorenz expression $(n^2-1)/(n^2+2)$, the author calculates refractivity constants R_ω and R_ϵ for the two principal refractive indices ω and ϵ, and finds that, in a number of cases, the ratio of these constants is almost exactly equal to the reciprocal of the crystallographic axial ratio in the corresponding directions in the crystal structure. Thus in the case of carbamide (tetragonal scalenohedral), $R_\omega/R_\epsilon = 0.834$, $a:c = 0.833$; in pentaerythritol (ditetragonal pyramidal), $R_s/R_\epsilon = 1.07$, $a:c = 1.024$; and in mellite, $C_6(CO_2)_6Al_2,18H_2O$ (ditetragonal bipyramidal), $R_\omega/R_\epsilon = 1.046$, $a:c = 1.055$. A similar relation holds in the double propionates of calcium with strontium and lead, and in isomorphous mixtures of the latter with the corresponding cubic calcium–barium double salt. It is pointed out that the refraction ratios, as well as the crystallographic axial ratios, are connected with the spacing of the planes of atoms in the space-lattices of the substances, and that comparison of the two ratios may be expected to throw light on the type of space-lattice represented in each case. Skeleton space-lattices are suggested for the above-mentioned substances. A

number of exceptions to the rule of inverse proportionality occur
In some cases the deviation is due to an incorrect choice of axial
ratios; in others it may be attributed to the presence of asymmetric
carbon atoms or to atomic anisotropism.   E. H. R.

**Liquid Crystals of the Hydrates of 10-Bromophenanthrene-
3- or -6-Sulphonic Acid.** O. LEHMANN (*Ann. Physik.*, 1918, [iv],
55, 81—102).—In the solid state, the compound forms thin leaflets
belonging apparently to the rhombic system, only slightly soluble
in hydrochloric acid, from which it was recrystallised, easily soluble
in alcohol, but with decomposition and separation of slender needles.
The compound forms two liquid crystalline hydrates with water,
the one with little water being slimy or gelatinous, that with more
water forming separate liquid crystalline drops. The two forms
appear to form mixed crystals to a limited extent. The liquid
drops have been examined microscopically in great detail, both with
ordinary and polarised light, and numerous diagrams are given
illustrating the appearance of the drops under different conditions.
The observations are held to support the author's theory of the
molecular isomerism of the different modifications of a substance,
as opposed to other theories of the relationship between amorphous
and crystalline forms.   E. H. R.

Colloidal Phenomena and the Adsorption Formula.
JOHN A. WILSON and WYNNARETTA H. WILSON (*J. Amer. Chem.
Soc.*, 1918, **40**, 886—895).—The theory of the mechanism of
protein swelling put forward by Procter and Wilson (T., 1916,
109, 307) is further developed, and the commonly used empirical
adsorption formula is discussed in relation to the theory.
It is shown that chemical combination of a colloid jelly with an
electrolyte to form an ionised colloid salt will cause the jelly to
swell to a maximum, which is followed by a gradually increasing
contraction as the concentration of the electrolyte in the solution is
increased.   If an electrolyte which does not combine with the
protein is added to the system, contraction of the swollen jelly takes
place to an extent which depends on the resulting ionic concen-
tration.
It is further shown that if the chemically combined electrolyte
and the total quantity of electrolyte in the jelly are represented as
functions of the concentration of the electrolyte in the external
solution, curves are obtained which are of the same form as those
which correspond with the empirical adsorption formula.
The microscopic pores found in certain hardened jellies are con-
sidered in relation to the continuity of the jellies regarded as two-
phase systems.   H. M. D.

Water-in-Oil Emulsions. ALFRED ULRICH MAX SCHLAEPFER
(T., 1918, **113**, 522—526).—With the aid of finely divided carbon
as emulsifier, it is possible to make emulsions of water in kerosene,
turpentine, benzene, toluene, and other liquids which wet the solid

more readily than water does. The results of experiments with varying proportions of kerosene and water are described, and it is shown that the viscosity of the emulsions increases with the amount of water which they contain. In no circumstances was it found possible to obtain emulsions with water as the external phase. The emulsifying action of the carbon depends on the fact that the oil-wetted carbon particles form a skin over the water droplets, and thus prevent their coalescence.

Carron oil is an emulsion of the water-in-oil type, and mixes freely with organic solvents, but not with water without shaking.

H. M. D.

Equilibrium in the System : Ferrous Carbonate, Carbon Dioxide, and Water.
HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 879—883).—The solubility of ferrous carbonate in aqueous solutions of carbonic acid of varying concentration has been measured at 30°. The experiments were carried out in a steel bottle, which was agitated for several days to ensure the attainment of equilibrium. The ferrous carbonate was prepared by the interaction of equimolecular quantities of ferrous sulphate and sodium hydrogen carbonate at 100° in aqueous solution saturated with carbon dioxide at a pressure of about 30 atmospheres.

The concentrations of the dissolved ferrous salt and carbon dioxide are found to satisfy the relation

$$\alpha[\mathrm{Fe(HCO_3)_2}]/\sqrt[3]{[\mathrm{H_2CO_3}]}=K,$$

in which α represents the degree of ionisation of the ferrous hydrogen carbonate, which has been assumed to be the same as that of barium nitrate in equivalent concentration. The average value of K is $4\cdot04\times10^{-3}$. Since the above theoretical constant $K=\sqrt[3]{K_1K_3/4K_2}$, where K_1 and K_2 are the first and second ionisation constants for carbonic acid and K_3 is the ionic solubility product for ferrous carbonate, it is possible to calculate K_3. Putting $K_1=3\cdot75\times10^{-7}$ and $K_2=4\cdot91\times10^{-11}$, this equation gives $K_3=34\cdot53\times10^{-12}$. From this it follows that, in the absence of hydrolytic decomposition, the solubility of ferrous carbonate in pure water would be $5\cdot8\times10^{-6}$ gram-molecules per litre.

H. M. D.

Equilibrium in the System : Zinc Carbonate, Carbon Dioxide, and Water.
HERBERT J. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 883—885).—The experiments were carried out in exactly the same way as those referred to in the preceding abstract. The zinc carbonate was prepared from the purest commercial product, which was treated with successive large quantities of boiling water. The basic carbonate was then subjected to the prolonged action of an aqueous solution of carbon dioxide under a pressure of about 30 atmospheres.

The quantities of zinc carbonate dissolved by carbonic acid solutions of varying concentration at 25° and 30° are in agreement

14*

with the formula $a[Zn(HCO_3)_2]/\sqrt{[H_2CO_3]} = 3\cdot36 \times 10^{-3}$, where a is assumed to have the same value as for zinc chloride.

From this value of the equilibrium constant and the ionisation constants for carbonic acid, the ionic solubility product, $K_3 = [Zn\cdot\cdot][CO_3{''}]$, is found to be 21×10^{-12} at 25°. In the absence of hydrolysis, the solubility of zinc carbonate in pure water at 25° would therefore be $4\cdot58 \times 10^{-6}$ gram-molecule per litre.

H. M. D.

Application of the Mass Law to the Process of Disinfection, being a Contribution to the Mechanistic Theory as Opposed to the Vitalistic Theory. RICHARD EDWIN LEE and C. A. GILBERT (*J. Physical Chem.*, 1918, **22**, 348—372).—An historical account of the development of the existent theories of disinfection is given, and the various theories, grouped into the two classes vitalistic theories and mechanistic theories, have been subjected to criticism in the light of data accumulated by a number of workers, obtained independently in many places and from some new experimental data of the authors. The velocity of disinfection has been determined in the case of *Bacillus typhosus* with phenol at $37\cdot5^\circ$, anthrax spores with mercuric chloride at 20°, and *Staphylococcus pyogenes aureus* with phenol at 20°. In all cases, the disinfectant had a concentration of $0\cdot2\%$. The velocity of reaction was determined by a modification of the Rideal-Walker drop method. A suitable quantity of the diluted broth culture of the micro-organism under examination was put into a test-tube containing a quantity of disinfectant solution of known concentration, and then placed in an incubator. After successive definite time intervals, accurately measured portions were transferred to Petri dishes and "plated," incubated, and the surviving organisms counted. The authors are of the opinion that the experimental evidence makes it probable that disinfection is an orderly time process which is closely analogous to a chemical reaction, the micro-organisms and the disinfectants being regarded as the respective reagents. A definite logarithmic relationship between velocity of disinfection and concentration has been found to exist in all cases investigated. Confirmation of the foregoing is furnished by the fact that the velocity of disinfection is influenced by variations in temperature and concentration in a manner in accord with the mass law. The explanation why disinfection is not sudden, but takes place according to the mass law, is as follows. Owing to changes in bacterial constituents, only a certain number of individuals are in a condition to be attacked by the disinfectant at a given time, but the total number of individuals in such a condition at any given moment represents a constant proportion of the surviving micro-organisms. The author considers the objections to the mechanistic theory put forward by Reichenbach (*Zeitsch. Hygiene*, 1910, **10**, 237), and points out that it is not necessary to regard disinfection as a reaction of the first order, but rather, as is pointed out by Nernst, as a reaction of **a higher order. The**

theory of graded resistance advanced by Eykman, Hewlett, and Reichel (A., 1909, ii, 1045; *Biochem. Zeitsch.*, 1908, **11**, 12) is criticised, and it is shown that the biological characteristics are distributed as a rule in a manner quite different from that assumed in the formation of the theory. In view of these observations, the authors are led to the conclusion that the logarithmic nature of disinfection is due to a general similarity of the individuals in a given pure culture rather than to a dissimilarity of the individuals as postulated in the theories of graded resistances by the supporters of the vitalistic theory. The authors also point out that although the work of Chick and Martin, and of Browning and Gilmour (*J. Path and Bact.*, A., 1913, i, 1138), indicates the specificity of disinfectants, this behaviour is to be expected if the disinfection process is analogous to chemical action, for in the application of the principle of the mass law the influence of the affinity factor is always taken into account. J. F. S.

Catalysis. IX. Calculation in Absolute Measure of Velocity Constants and Equilibrium Constants in Gaseous Systems. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1918, **113**, 471—492).—The concept of critical energy and critical increment in connexion with the formation of active molecules is further considered, and it is shown that reaction velocities and equilibrium constants may be calculated on the basis of molecular statistical considerations. Expressions are derived for the velocity of a unimolecular reaction and of bimolecular reactions in which the reacting molecules are of the same kind and also of different kinds. The theoretical treatment includes a consideration of the reaction velocity formulæ in the light of the radiation hypothesis.

The formulæ derived are applied to a number of gaseous reactions which have been experimentally examined, such as the decomposition of hydrogen iodide, the combination of hydrogen and iodine, and the dissociation of iodine, bromine, chlorine, and hydrogen, and it is shown that the calculated results are in fair agreement with those found by experiment. The formulæ may be used for the calculation of velocity or equilibrium constants in regions which do not admit of experimental determination by reason of the extremely high or low velocities which are involved.

The question of the unimolecular decomposition of hydrogen iodide is discussed, and it is shown that the velocity is very small compared with that of the bimolecular change at all temperatures at which this reaction has been examined experimentally. Calculation indicates, however, that the two velocity constants should be of the same order of magnitude in the neighbourhood of 1200° (abs.). At this temperature, the progress of the reaction would consequently not be satisfactorily represented by the equation for a bimolecular change. H. M. D.

Periodic System of the Elements. STEFAN MEYER (*Physikal. Zeitsch.*, 1918, **19**, 178—179).—The author gives two methods of

representing the periodic classification, in the first of which each series is written out at length and arranged in such a way that the eighth group elements lie in the centre of the scheme; to the right the elements of groups 1, 2, 3, etc., in order, and to the left the elements 7, 6, 5, etc. This arrangement places the elements of smallest atomic volume in the centre, so that passing either to the left or right of the centre is accompanied by an increase of atomic volume.   In the second arrangement, the alkali metals occupy the middle of the table; to the right the groups follow 2, 3, 4 . . . 8, with + valencies 2—8, and to the left the groups 0, 7, 6 . . . 1, with −valencies 0—7. This arrangement places the elements with largest atomic volume in the centre, and on passing either to the right or left of the centre there is a decrease in atomic volume. The author places both the atomic weights and the atomic numbers alongside the elements. In the first arrangement, the elements of the rare earth group are placed together in groups III and IV to the left of the table, whilst in the second arrangement they are spread out in various groups in the third and fourth long series, although in this case the author definitely states that their positions are not definitely fixed.   J. F. S.

The " De-salting " of Sea-water. WALTER BRIEGER (*Chem. Zeit.*, 1918, **42**, 302. Compare A., 1911, ii, 723).—Quotations are given from ancient and modern literature to show that sea-water is not freed from salt by passing it through porous earthenware, as stated by Aristotle.   W. P. S.

New Simple Ultra-filters. II. Spontaneous Ultra-filters. WOLFGANG OSTWALD (*Kolloid Zeitsch.*, 1918, **22**, 143—147. Compare this vol., ii, 192).—The efficiency of the ultra-filters which have been previously described has been found to depend on the presence of moisture in the filter paper which is used in the preparation of the filters. Dry filter paper does not give nearly such satisfactory results as filter paper which contains appreciable quantities of moisture. By treatment of moist filter paper with 2% collodion solution in the manner previously described, ultra-filters are obtained which show a markedly increased rapidity of action. Such ultra-filters may be used without the application of external pressure as an aid to filtration. The observed differences in the efficiency of ultra-filters made with dry and moist filter paper are attributable to differences in the structure of the collodion membrane in the two cases. The greatly increased filtering surface which is obtained when moist filter paper is used may be accounted for in terms of the structural peculiarities which are exhibited by the collodion membrane formed at the surface of water.
                                                                    H. M. D.

Simplified Short Vacuum Gauge. ENOCH KARRER (*J. Amer Chem. Soc.*, 1918, **40**, 928—929).—A modified short Gaede gauge is described in which the connexion between the adjustable mercury receiver and the exhausted space is made through a steel tube

which is welded to a tube of platinum foil, which in turn is fused into the lower end of the glass gauge tube. This is silvered and then copper-plated, and the seam in the platinum foil is then rendered gas-tight by a layer of solder bridging the copper-plated glass surface and the surface of the steel tube.   H. M. D.

Inorganic Chemistry.

Hydrogen Ion Concentrations of Various Indicator Endpoints in Dilute Sodium Hypochlorite Solutions. GLENN E. CULLEN and J. HAROLD AUSTIN (*J. Biol. Chem.*, 1918, **34**, 553—568).—The end-points of indicators in dilute sodium hypochlorite solutions are different from the end-points of the same indicators in ordinary solutions, on account of the bleaching action of the hypochlorite. The end-point to powdered phenolphthalein in a 0·5% sodium hypochlorite solution is at a P_H of about 10·1, whilst in an alcoholic solution of *o*-cresolphthalein it is at a P_H of about 9·3. The latter indicator gives an end-point in 1% sodium hypochlorite solution at about P_H 9·6. In the preparation of Dakin's hypochlorite solution (A., 1915, i, 924), the authors recommend that chlorine should be passed into a sodium carbonate solution containing 14 grams to the litre until sodium hypochlorite is formed in a concentration of 0·5%, as shown by titration with thiosulphate. H. W. B.

Absorption of Atmospheric Gases by Water. II. A Diagram showing the Volume of Oxygen dissolved by Water at Different Temperatures and Pressures. Additions to the Bibliography. J. H. COSTE (*J. Soc. Chem. Ind.*, 1918, **37**, 170—171T. Compare A., 1917, ii, 463).—To facilitate the calculation of the volume of oxygen dissolved in water, the author has constructed a series of graphs which give the number of c.c. of oxygen dissolved in 1 litre of water at temperatures from 0° to 25° and pressures from 710 mm. to 780 mm. An additional bibliography is added to the paper. J. F. S.

Effect of Acetylene on the Oxidation of Ammonia to Nitric Acid. GUY B. TAYLOR and JULIAN H. CAPPS (*J. Ind. Eng. Chem.*, 1918, **10**, 457—459).—The presence of a small quantity of acetylene in the ammonia–air mixture has a deleterious effect on the platinum catalyst; with 0·02% of acetylene, the yield falls from 95% to 89% or less, whilst 0·1% of acetylene decreases the yield to 65%. Ammonia gas may be freed from acetylene and other non-reacting gases by dissolving it in water to form a concentrated solution and then vaporising the latter with air. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Density, Compressibility, and Atomic Weight of Argon. A. LEDUC (*Compt. rend.*, 1918, **167**, 70—71).—Working with a carefully purified sample of argon, the author finds for its density the value 1·3787, for its coefficient of departure from Mariotte's law between 1 and 5 atmos., at 14° the value $10·2 \times 10^{-6}$, and for its atomic weight the value 39·91. W. G.

The Reaction between the Alkali Phosphates and Magnesium Chloride. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **102**, 241—246).—The author has examined the precipitates formed by bringing together under different conditions magnesium chloride and disodium, dipotassium, or dirubidium hydrogen phosphate. Generally, magnesium monohydrogen phosphate is precipitated, with a variable content of water of crystallisation, but it is liable to be contaminated with magnesium monoalkali phosphate, and under suitable conditions the whole of the precipitate may be formed of the latter type of salt. Thus, when a dilute solution of magnesium chloride is added slowly with agitation to a 10% solution of dipotassium hydrogen phosphate, the salt $MgKPO_4,6H_2O$ is precipitated in an almost pure condition, but if the solutions are mixed in the reverse order, the precipitate is of uncertain composition, containing variable quantities of $MgKPO_4$ aq., $MgHPO_4$ aq., $Mg(OH)_2$, and $Mg_3(PO_4)_2$. The rubidium salt, $MgRbPO_4,6H_2O$, can be precipitated almost pure in a similar manner to the potassium salt.

The work of Fröschel has shown (*Ber. Südslav. Akad.*, 1912, **190**, 117—138) that in whatever manner dilute solutions of magnesium chloride and disodium hydrogen phosphate are mixed, equilibrium between the products of reaction is eventually obtained. Fröschel omitted to observe, however, that the precipitate is not pure $MgHPO_4$ aq., but liable to be contaminated with magnesium alkali phosphate. The author quotes analyses showing that when saturated solutions of these salts are mixed, the precipitate contains a considerable quantity of alkali. The results explain the reason for the supposed existence of so many hydrates of $MgHPO_4$, and also emphasise the danger of the presence of alkali cations during the estimation of phosphoric acid by the magnesium ammonium phosphate method. E. H. R.

Isotopic Lead. FRANK WIGGLESWORTH CLARKE (*Proc. Nat. Acad. Sci.*, 1918, **4**, 181—188).—The constancy of the atomic weight of lead from non-radioactive minerals and its independence on the species and locality of the mineral suggest that ordinary lead is a distinct variety, not a balanced mixture of the isotopes derived from uranium and thorium. The very variable atomic weight of lead derived from uranium minerals suggests that this "normal" or ordinary lead is present in varying amount along with the isotope derived from uranium. A hypothesis of elementary evolution is suggested, in which ordinary lead is a product of evolution the lighter elements condensing in the processes into the heavier

elements, and the isotopes formed in radioactive change are products of degradation or decay. The atom being a very highly complex structure, in which the constituents must come together in irregular proportions, the process of evolution from the lighter to the heavier forms is regarded as a slow process in which the final stable configuration is not at once attained, but only after a period of selection of the constituent parts.   F. S.

Mercury Hydrosols produced from Metallic Mercury. IVAR NORDLUND (*Diss., Upsala*, 1918, 1—125).—The preparation of mercury sols has been studied by a variety of methods, which include (*a*) mechanical dispersion methods, (*b*) thermal dispersion methods, and (*c*) electrical dispersion methods. Under the first group of methods, it is shown that by spirting a fine stream of mercury by means of high pressure into solutions of potassium nitrate and gelatin, definite sols of mercury are produced, although the particles are relatively large. With solutions of ammonia, ammonium chloride, ammonium sulphate, or carbamide, or even pure water, no sol-formation occurred by this method. When mercury is shaken with pure water or with dilute solutions of potassium chloride, sodium chloride, potassium nitrate, potassium sulphate, copper sulphate, mercurous nitrate, or acetic acid, there is no formation of colloidal mercury, but if dilute solutions (ca. $10^{-5}N$) of ammonia, ammonium sulphate, ammonium chloride, calcium citrate, tartaric acid, potassium tartrate, carbamide, or gelatin are used, definite colloidal solutions are produced. Mercury sols are also produced by passing hot mercury vapour directly into water. Mercury sols can be readily prepared by the Bredig method of electrical dispersion, using either direct or alternating current. The law of Stokes is tested for the velocity of fall of a mercury drop through an 11% solution of water in glycerol, and the results show that within the limits of experimental error the law holds for this case. The various sols have been examined in connexion with the distribution of the particles. The sols have varying colours from grey to yellowish-brown and reddish-brown; to characterise the colour of the sols more exactly, the absorption spectrum has been determined over the range $\lambda = 253$---$263 \mu\mu$. A number of experiments are described on methods of estimating the purity of the sols produced in different ways, the stability toward various electrolytes, and the stabilising action of electrolytes. From kataphoresis experiments, it is shown that the sols are all positively charged except those prepared in citrate and tartrate solutions, which are negatively charged.   J. F. S.

The Chemistry of Quinquevalent Tungsten. OSCAR O : SON COLLENBURG (*Zeitsch. anorg. Chem.*, 1918, **102**, 247—276).—By the reduction of tungstic acid or a tungstate in oxalic acid solution with tin, the author has succeeded in preparing soluble, fairly stable complex oxalates containing quinquevalent tungsten. These salts have been isolated in a pure condition, and from them other

compounds containing quinquevalent tungsten have been prepared. The reduction with tin proceeds smoothly only in the one stage. It is best to reduce a solution of an alkali tungstate in a concentrated solution of oxalic acid containing slight excess of alkali oxalate. The course of the reduction can be followed by the colour change, through dark blue, green, and yellow to deep red. After removal of tin and excess of oxalic acid, the complex oxalate is precipitated by means of alcohol, and can be purified by dissolving in hot water and salting out, the sodium salt with sodium bromide, the potassium salt with potassium iodide. The compounds must be dried in a current of carbon dioxide, but are fairly stable in air when dry. The sodium salt has the composition $3Na_2O,2W_2O_5,4C_2O_3,12H_2O$, and the potassium salt

$$3K_2O,2W_2O_5,4C_2O_3,9H_2O.$$
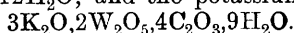
They are red, crystalline powders which slowly oxidise in air, and at $100°$ lose their water, but do not decompose. They are very soluble in water, insoluble in organic solvents. Sodium hydroxide in the cold precipitates from their aqueous solution a brown, amorphous substance containing quinquevalent tungsten, but on boiling, part of this dissolves to form a tungstate, whilst a dark residue remains, probably containing quadrivalent tungsten. The complex oxalates can be regarded as *oxalotungstites*, derived from a hypothetical tungstous acid.

The oxalotungstites dissolve in concentrated hydrochloric acid, forming a deep blue solution, which contains an *oxychloride* of quinquevalent tungsten, probably $WOCl_3$. From this solution, complex chlorides can be isolated containing $WOCl_3$ in combination with chlorides of the alkali metals or ammonium or hydrochlorides of organic bases. The ammonium and potassium salts are precipitated by saturating a hydrochloric acid solution of the corresponding oxalotungstite with hydrogen chloride. The rubidium, cæsium, aniline, tetraethyl- and tetrapropyl-ammonium compounds are precipitated when the corresponding chloride is added to a hydrochloric acid solution of an oxalotungstite, and the pyridine and quinoline compounds are prepared by double decomposition of their hydrochlorides with ammonium chlorotungstite. Four types of complex chlorides have been observed. Type Ia has the composition M_2WOCl_5, in which M may be NH_4, Rb, Cs, or $C_6H_5NH_3$; type Ib, M_2WOCl_5,xH_2O, is represented by the potassium compound; type IIa, $MWOCl_4$, is represented by the pyridine and quinoline compounds, and type IIb, $MWOCl_4,H_2O$, by tetraethyl- and tetrapropyl-ammonium compounds. The compounds of type I correspond with the so-called molybdenyl chlorides; they form green crystals. Those of type II have no representative among molybdenum compounds; they form shining, brown crystals (IIa) or bright, greenish-blue crystals (IIb). The latter hold their water with great tenacity, and may be regarded as hydroxy-compounds, for example, $(C_2H_5)_4N,W(OH)_2Cl_4$. The author prefers to regard the compounds as chloro-derivatives of tungstous acid, rather than as double chlorides or tungstyl chlorides,

those of type II being derived from *metatungstous acid*, WO_2,OH, and those of type I from the hydroxide, $W(OH)_5$

The *chlorotungstites* are stable in dry air at the ordinary temperature, but decompose with oxidation to tungstates at 60—70°. They are immediately hydrolysed by water with formation of a brown hydroxide, which has not been analysed. The less soluble cæsium compound is, however, far more stable than the readily soluble ammonium and potassium compounds. They dissolve readily in absolute methyl and ethyl alcohols, with the exception of the rubidium and cæsium compounds, but not in other organic solvents. Concentrated hydrochloric acid and 35% sulphuric acid also dissolve them, but alkalis and ammonia decompose them. Oxidising agents convert them into tungstates, and permanganate and iodine have been employed for quantitative determinations of the quinquevalent tungsten.

The chlorotungstites react vigorously with a concentrated solution of potassium cyanide with evolution of hydrogen cyanide. A reddish-yellow solution is formed containing cyanides of the type $M_4W(CN)_8$, from which a sparingly soluble cadmium compound, $Cd_2W(CN)_8,8H_2O$, has been isolated. A thiocyanic acid compound has also been isolated in the form of a pyridine salt having the composition $(PyH)_2WO(SCN)_5,xH_2O$.

Full details for the preparation of each of the chlorotungstites described are given.   E. H. R.

Behaviour of Solutions of Stannic Fluoride. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 906—914).—Stannic fluoride was prepared by the action of anhydrous hydrogen fluoride on stannic chloride according to the method of Ruff and Plato by the use of apparatus involving a minimum amount of platinum. According to observations on the electrical conductivity of its solutions, it hydrolyses much less rapidly than stannic chloride. The conductivity increases rapidly at first, but attains a constant value after some days. The final value corresponds closely with that calculated on the assumption that complete hydrolysis takes place in accordance with the equation $SnF_4 + 4H_2O = Sn(OH)_4 + 4HF$.

Experiments made with a view to ascertain the amount of hydrofluoric acid which is necessary to prevent the precipitation of tin by the action of hydrogen sulphide show that the hydrogen ion concentration must be such that hydrolysis of the stannic fluoride becomes inappreciable. The anomalous behaviour of stannic tin in hydrofluoric acid solution may be explained either by the assumption that stannic fluoride has little tendency to ionise, or by the formation of complex ions of the type H_nSnF_{4+n}. Of the two hypotheses, the former seems to be in better agreement with the facts.   H. M. D.

Combinations of Normal Zirconyl Sulphate with some Alkali Sulphates (K,Na,NH₄). ED. CHAUVENET and (MLLE.) H. GUEYLARD (*Compt. rend.*, 1918, **167**, 24—25. Compare this vol.,

ii, 234).—Normal zirconyl sulphate forms compounds of the types $(ZrO \cdot SO_4)_3, X$ or $(ZrO \cdot SO_4)_3, X_2$, where X may be ZrO_2 or an alkali sulphate. The compounds which have been isolated are

$$(ZrO \cdot SO_4)_3, K_2SO_4, 8H_2O,$$

$(ZrO \cdot SO_4)_3, 2Na_2SO_4, 7H_2O$, and $(ZrO \cdot SO_4)_3, 2(NH_4)_2SO_4, 7H_2O$.

W. G.

Chemistry of Gold at High Temperatures and Pressures.

HAROLD H. MORRIS (*J. Amer. Chem. Soc.*, 1918, **40**, 917--927). --In reference to the explanation of the occurrence of free gold in nature, experiments have been made on the behaviour of gold compounds under the influence of water at high temperatures and pressures. The experiments were made with a specially constructed steel bomb. Gold hydroxide yields metallic gold when treated with water at 322°. In presence of sodium chloride and magnesium chloride, decomposition takes place at a lower temperature; calcium chloride, on the other hand, tends to prevent the decomposition.

Gold chloride may be heated to the critical temperature (370°) before metallic gold appears. In presence of small quantities of sodium, magnesium, or calcium chloride, gold chloride is more stable, and reduction to the metal is not observed until the temperature is raised to 450—460°. The increased stability is attributed to the formation of double chlorides.

Calcite and magnesite become plated with gold when heated with gold chloride solutions up to 310°. Sodium, magnesium, and calcium chlorides prevent this action from taking place until the temperature is raised to about 500°.

Magnesium hydrogen carbonate acts like the normal carbonate, but calcium hydrogen carbonate appears to have no influence on the stability of a gold chloride solution.

It has also been observed that gold dissolves in hot hydrochloric acid containing auric chloride. Aurous chloride is formed.

H. M. D.

Mineralogical Chemistry.

The Constitution of Coal. MARIE C. STOPES and R. V. WHEELER (*Dept. Sci. Ind. Research*, 1918, 1—58).—A monograph in which the subject is dealt with both from the economic and scientific points of view. The points considered are the definition of coal and its general constitution, the principal methods of accumulation of coal-forming vegetable material, the action of solvents on coal, the destructive distillation and distillation at different temperatures, the nature of the liquid distillates, the microscopical evidence on the constitution of coal, the nature of

the "ulmic substances," the action of reagents on coal, and the nature of artificial coals. There is a brief discussion of the various theories on the constitution of coal, an appendix on the classification of coals, and a very full bibliography. W. G.

Augite from Stromboli. S. Kozu and H. S. Washington (*Amer. J. Sci.*, 1918, [iv], **45**, 463–469).—Dull, black, or brownish-black crystals of augite about 1 cm. long occur loose in some abundance in the volcanic ash around the crater of Stromboli. $D^{19°}$ 3·243. The refractive indices ($\alpha_{Na} = 1·693$, $\beta = 1·699$, $\gamma = 1·719$) are lower than are usual for augite, corresponding with the preponderance of the diopside molecule shown by the following analysis. This analysis (I) corresponds with $Ca(Mg,Fe)Si_2O_6$ 80·12, $(Mg,Fe)SiO_3$ 7·48, $(Mg,Fe)Al_2SiO_6$ 7·03, $NaFeSi_2O_6$ 5·46%. Analysis II is of the basalt scoria in which the crystals occur.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	NiO.	MgO.
I.	50·94	0·96	3·37	2·05	7·41	0·10	n.d.	14·59
II.	50·83	0·81	16·66	1·52	6·64	0·12	n.d.	6·08

	CaO.	SrO.	Na_2O.	K_2O.	P_2O_5.	H_2O.	Total.
I.	20·34	0·08	0·61	0·18	—	0·08	100·71
II.	10·99	—	2·66	2·05	1·61	0·36	100·33

L. J. S.

Analytical Chemistry.

Universal Gasometer. JAROSLAV MILBAUER (*Zeitsch. anal. Chem.*, 1918, **57**, 161—162).—The apparatus described allows the gas contained in it to be delivered at any predetermined rate and constant pressure, the water being admitted through an adjustable constant-level device. W. P. S.

Mercuric Oxide as a Standard for Volumetric Analysis. G. INCZE (*Zeitsch. anal. Chem.*, 1918, **57**, 176).—A reply to Rosenthaler (this vol., ii, 236). The author's method for using mercuric oxide differs from that described by Rosenthaler and Abelmann. W. P. S.

Estimation of Halogens, Sulphur, and Nitrogen in the Presence of Mercury. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **166**, 1000—1003).—For the estimation of halogens, the mercury is removed by means of zinc turnings by the method previously described (compare this vol., ii, 276), but without using potassium iodide, all the filtrates and decanted liquids being kept and mixed,

and in this solution the halogens are estimated by means of silver nitrate in the usual manner.

For the estimation of sulphur, this is first converted into sulphate by oxidation with bromine in hydrobromic acid, and then the mercury and excess of bromine are removed by the addition of zinc turnings, the sulphur being estimated in the filtrate by pre cipitation as barium sulphate.

Nitrogen in the form of mercuriammonium or mercuriamino-compounds is estimated in the filtrate, after the removal of mercury by the method described (loc. cit.), by addition of alkali and distillation of the ammonia or amine into dilute hydrochloric acid and weighing as ammonium chloride or amine hydrochloride.

W. G.

Volumetric Estimation of Chlorine, Bromine, Cyanogen, and Mercury. EMIL VOTOČEK (Chem. Zeit., 1918, **42**, 271—272. Compare this vol., ii, 238).—The method described for the titration of chlorides may also be applied to bromides and cyanides, but not to iodides or fluorides; conversely, it may be used for the volumetric estimation of mercury. The insolubility of cupric nitroprusside affords a means of separating this metal from mercury, since mercury nitroprusside is soluble in the presence of an excess of sodium chloride. [See, further, J. Soc. Chem. Ind., 444A.]

W. P. S.

Estimation of Combined Chlorine in Gastric Juice. GEORGES and FABRE (Soc. Pharm. Paris, 1917; from Ann. Chim. anal., 1918, **23**, 133—134).—Five c.c. of the sample are heated with 10 c.c. of $N/10$-silver nitrate solution, 6 c.c. of saturated potassium permanganate solution, and 10 c.c. of nitric acid; the excess of silver nitrate is then titrated with thiocyanate solution. This gives the total chlorine. Another portion of 5 c.c. of the sample is evaporated in a platinum basin, and the combined chlorine is estimated in the residue as described. The fixed (inorganic chlorine) is estimated in the ash of the sample. Three specimens of gastric juice contained 2·99, 2·84, and 1·09 grams of fixed chlorine per litre, respectively.   W. P. S.

Detection of Iodides in the Presence of Cyanides. L. J. CURTMAN and C. KAUFMAN (J. Amer. Chem. Soc., 1918, **40**, 914—917).—Comparative experiments made on the detection of iodide in presence of relatively large quantities of cyanide with potassium nitrite, potassium permanganate, hydrogen peroxide, and chlorine as oxidising agents show that the interference of cyanide is least when permanganate is used as the oxidising agent.

If the cyanides are precipitated by the addition of cobalt nitrate and the filtrate examined for iodide by the use of permanganate, sulphuric acid, and chloroform, it is possible to detect 1 part of iodide in presence of 500 parts of cyanide. [See J. Soc. Chem. Ind., 413A.]   H. M. D.

The Microchemical Method of Estimating Residual Nitrogen. IVAR BANG (*Biochem. Zeitsch.*, 1918, **87**, 259—263).— The urea can be first extracted from the blood sample on filter paper by treatment with alcohol–ether mixture for five hours, and the remaining nitrogen is then extracted with phosphomolybdic acid solution (0·05% phosphomolybdic acid + 1·5% sulphuric acid) for one hour. The nitrogen in each extract is estimated by the micro-Kjeldahl method. S. B. S.

Detection of Nitrates in Water. ESCAÏCH (*J. Pharm. Chim.*, 1918, [vii], **17**, 395).—Fifteen c.c. of the water are mixed with 2 c.c. of 10% antipyrine solution and 4 drops of acid mercuric sulphate solution, and a drop of 5% potassium ferricyanide solution is added. In the presence of 0·1 mg. of nitrite per litre of water, a red coloration is obtained. The reaction is characteristic of nitrites and may be used for the detection of nitrates after these have been reduced by "amalgamated" aluminium. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Simplified Working with a Nitrometer. RUDOLF KAESBOHRER (*Chem. Zeit.*, 1918, **42**, 296).—In the usual gasometric estimation of nitric acid, an approximate correction is made for the pressure due to the acid layer, a depth of 7 mm. of acid being taken as equivalent to 1 mm. of mercury. A more trustworthy procedure is to bring the mercury to the same level in the measuring and levelling tubes, read the volume of the gas, open the tap of the measuring tube, and note the difference in level of the mercury. This difference in mm. is subtracted from the barometric pressure during the experiment. W. P. S.

Estimation of Nitric Acid in Bismuth Subnitrate. E. LUCE (*Bull. Soc. chim.*, 1918, [iv], **23**, 264—271; *J. Pharm. Chim.*, 1918, [vii], **17**, 349—359).—At 95° bismuth subnitrate reacts with oxalic acid in the presence of manganese sulphate according to the equation $6(C_2H_2O_4,2H_2O) + 2(BiO\cdot NO_3) + H_2SO_4 = 2NO + 3CO + 9CO_2 + 19H_2O + (BiO)_2SO_4$. About 0·5 gram of bismuth subnitrate and 1 gram of manganese sulphate are heated in a flask under a reflux apparatus for one and a-half hours with 50 c.c. of a solution containing 20 grams of crystallised oxalic acid and 60 c.c. of sulphuric acid per 100 c.c.; to prevent secondary reactions, a current of carbon dioxide must be passed through the flask during the reaction. The excess of oxalic acid is then titrated with standardised permanganate solution. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

Critical Elaboration of Quantitative Precipitation Methods Exemplified by a Method for the Estimation of Phosphoric Acid. H. HEIDENHAIN (*J. Ind. Eng. Chem.*, 1918, **10**, 426—429).—To determine whether a method is trustworthy, it is necessary to know the solubility of the precipitate and the

influence of concentration, temperature, presence of other substances, etc. The purity of the precipitate also requires investigation. In the estimation of phosphoric acid by precipitation with molybdic acid and titration of the precipitate with sodium hydroxide solution, the presence of ammonia interferes with the endpoint when phenolphthalein is used as the indicator. It is therefore recommended that the phosphoric acid should be precipitated as potassium phosphomolybdate and the precipitate washed with 10% potassium nitrate solution containing free nitric acid ($N/100$ strength). The small quantity of acid remaining in the filter can be estimated and a correction made. [See, further, *J. Soc. Chem. Ind.*, August.] W. P. S.

The Wet Method for Estimation of Carbon. WILHELM STEPP (*Biochem. Zeitsch.*, 1918, **87**, 135—142).—The author discusses the following points in the wet estimation: (*a*) The form of the apparatus. This is figured in the text, and the flask in which decomposition takes place is connected with a condenser to retain the acid. (*b*) The purification of the sulphuric acid. This is accomplished by heating it first with potassium dichromate, and afterwards with permanganate. (*c*) The purity of potassium dichromate used for oxidation of organic salts. It is difficult to obtain this quite free from carbonate. The author substitutes a mixture of chromic acid and sulphuric acid. Finally, when oxidation with the mixture of chromic and sulphuric acids has gone on for four hours, the apparatus is allowed to cool in a current of air free from carbon dioxide, and 10 c.c. of $5^0/_{00}$ solution of potassium permanganate are added, and the mixture is heated for another hour. S. B. S.

The Estimation of Carbonates and Hydrogen Carbonates in the Cold; Analysis of a Mixture of these Salts. Exact Details for the Use of Litmus and Phenolphthalein as Indicators. W. MESTREZAT (*Bull. Soc. chim.*, 1918, [iv], **23**, 250—254).—The author finds that in the titration of carbonates, using phenolphthalein as indicator, a satisfactory and correct endpoint is obtained when the whole of the carbonate is just converted by the acid into hydrogen carbonate, if the alkaline liquid is so diluted as not to contain more than 0·07% of sodium carbonate.

Similarly, total alkalinity may be determined by titration in the cold, using litmus as an indicator, if the procedure used is as follows. The standard acid is run in, 1—2 c.c. at a time, until a change in the tint of the indicator is just noticeable. Then between each successive addition of 0·2—0·3 c.c. of acid the liquid is mixed and divided into two parts, one being used as a control and the other receiving the acid. That point at which an addition of acid produces no colour change, as shown by the comparison, is the endpoint. W. G.

Estimation of Sodium and Potassium [in Foodstuffs, etc.]. S. N. RHUE (*J. Ind. Eng. Chem.*, 1918, **10**, 429—431).—The

sulphated ash of the substance is dissolved in hydrochloric acid, and after separation of phosphoric acid, iron, calcium, magnesium, etc., the sodium and potassium are weighed together as sulphates. The potassium is estimated in a separated portion of the ash by precipitation as potassium platinichloride after the iron and calcium have been removed. The potassium platinichloride is washed with 80% alcohol, then with 20% ammonium chloride solution saturated with potassium platinichloride (this removes magnesium sulphate and traces of calcium salts), and finally with 80% alcohol. [See, further, *J. Soc. Chem. Ind.*, August.]   W. P. S.

The Lawrence-Smith Method for the Estimation of Alkalis in Silicates. P. WENGER and ED. BRANGE (*Mon. Sci.*, 1918, [v], **8**, I, 97—99).—The Lawrence-Smith reaction for the decomposition of silicates (heating with a mixture of calcium carbonate, 8 parts, and ammonium chloride, 1 part) is complete when the mixture is heated for two hours at 700°. After cooling, the mixture is treated with water, filtered, the calcium is removed from the filtrate, and the alkalis then estimated in the usual way. [See, further, *J. Soc. Chem. Ind.*, August.]   W. P. S.

Detection of Strontium in the Presence of Barium by Calcium Sulphate Solution. THEODORA P. RAIKOW (*Zeitsch. anal. Chem.*, 1918, **57**, 164—170).—Although strontium sulphate forms slowly when a soluble strontium salt is treated with calcium sulphate solution, the presence of a barium salt, and consequent formation of barium sulphate, greatly increases the rate of precipitation of strontium salt. To detect strontium in the presence of barium, 10 c.c. of the solution to be tested are treated with an excess of calcium sulphate solution, the mixture shaken for fifteen seconds, and then filtered. If the filtrate becomes turbid after a short time, or does so when boiled, strontium is present. In cases where a turbidity is not obtained, the precipitate on the filter should be washed several times with hot water and the filtrate now tested with barium chloride solution; the washing dissolves out any strontium sulphate precipitated with the barium sulphate, and a turbidity is produced on the addition of barium chloride. W. P. S.

Precipitation of Magnesium as Oxalate and the Theory of the Formation of Precipitates. A. ASTRUC and J. CAMO (*J. Pharm. Chim.*, 1918, [vii], **17**, 381—386).—A discussion of the conditions affecting the precipitation of magnesium oxalate. The quantity of this oxalate which is precipitated from magnesium acetate solution by oxalic acid increases with the concentration of the acetate solution. In the separation of large quantities of magnesium salts from calcium salts, the calcium oxalate should be precipitated from a very dilute solution. [See, further, *J. Soc. Chem. Ind.*, August.]   W. P. S.

Hæmatoxylin as a Reagent for Copper Ions and Imperfect Complexes of Copper. S. REBELLO-ALVES and A. BENEDICENTI (*Arch. farm. sper. sci. aff.*, 1917, **24**, 50—57; from *Physiol. Abstr.*, 1918, **3**, 164).—To detect the presence of copper in protein complexes, the solution is treated with a drop of neutral red solution and then with a very dilute solution of sodium carbonate until a clear yellow is obtained, when the solution is sufficiently alkaline for the reaction between hæmatoxylin and copper.   S. B. S.

The Titration of Copper with Potassium Cyanide. M. P. APPLEBEY and K. W. LANE (*Analyst*, 1918, **43**, 268).—In titrating copper with potassium cyanide, the end-point of the reaction is no longer sharp in the case of solutions containing much less than 1 gram of copper per litre. A method of titrating amounts of about 0·1 gram per litre, however, has been based on the fact that a solution of a double carbonate of copper and an alkali in excess of sodium carbonate solution reacts sharply with cyanide, the end-point of the reaction being shown by the colour changing from blue to an unstable grey, the solution becoming clear and colourless in a few minutes. The double carbonate is prepared by adding the copper solution to a solution of sodium carbonate and sodium hydrogen carbonate, the presence of the latter being necessary to prevent the precipitation of a basic carbonate.

C. A. M.

Volumetric Estimation of Copper by Potassium Thiocyanate, Potassium Iodide, and Thiosulphate. G. BRUHNS (*Chem. Zeit.*, 1918, **42**, 301—302).—The presence of potassium thiocyanate is of advantage in the iodometric estimation of copper, since it decreases the amount of potassium iodide required. The cupric salt solution is treated with a small quantity of potassium iodide and then titrated with thiosulphate solution containing potassium thiocyanate. The latter reacts with the cuprous iodide first formed and liberates an equivalent amount of potassium iodide, which in turn reacts with a further quantity of the cupric salt. [See, further, *J. Soc. Chem. Ind.*, 446A.]   W. P. S.

A New Method of Estimating Mercury by means of Zinc Filings. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **166**, 950—952).—The mercury salt, in a finely divided state, is placed in a conical flask with 1 gram of zinc filings and 10 c.c. of 2N-sulphuric acid. After half an hour, a second quantity of zinc and acid is added, this being repeated at the end of the first hour. After twenty-four hours, the liquid is decanted through a filter and the residue washed four times by decantation with water. To it is then added, 5 c.c. at a time, 25 c.c. of dilute hydrochloric acid (1:1). After twenty-four hours, this liquid is decanted and 25 c.c. of fuming hydrochloric acid are added. After a further twenty-four hours, the zinc has all dissolved, and the mercury is in

the form of one large globule, which is carefully washed by decant-ation, transferred to a porcelain crucible, and dried first by filter paper and finally over sulphuric acid in the cold, and weighed. The method is accurate and applicable to all mercury salts except the sulphide, which must first be oxidised to the sulphate. It is advisable to add 0·5 gram of potassium iodide to the mercury salt before commencing the estimation. W. G.

The Use of Hydrofluoric Acid in Analysis. N. HOWELL FURMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 895—906).—A summary is given of the results which have been previously obtained by the use of hydrofluoric acid solutions in the separation of metals by electro-analysis and by precipitation as sulphides. Further results are given which show that copper can be quantitatively separated from vanadium in acid fluoride solution by electro-deposition of the copper. Vanadium thus behaves similarly to tin and tungsten, and preliminary observations indicate that uranium and titanium fall into the same category.

The general chemical behaviour of stannic tin in acid fluoride solutions shows that the stannic ion is not present in appreciable quantity, for such solutions give none of the characteristic reactions of stannic tin. In consequence of this behaviour, hydrofluoric acid may be conveniently used in the analysis of tin–antimony alloys. The procedure recommended is described in detail.

By the addition of boric acid to an acid fluoride solution of stannic tin, the ordinary chemical properties of the stannic ion are developed, and the tin may be quantitatively separated by the action of hydrogen sulphide or by electro-deposition. The boric acid may be replaced by silica with similar results. The action of the boric acid is presumably connected with the formation of borofluoride, and it is shown that acid fluoride solutions to which excess of boric acid has been added have comparatively little action on glass vessels.

The action of boric acid on the behaviour of tin in hydrofluoric acid solution is made the basis of a method for the qualitative analysis of the tin group of metals. [See also *J. Soc. Chem. Ind.*, 445A.] H. M. D.

Colorimetric Estimation of Lactose in Milk. AUGUST J. P. PACINI and DOROTHY WRIGHT RUSSELL (*J. Biol. Chem.*, 1918, **34**, 505—507).—A modification of Lewis and Benedict's colorimetric method for the estimation of dextrose in the blood (A., 1915, ii, 111) is described for the estimation of lactose in milk. [See, further, *J. Soc. Chem. Ind.*, August.] H. W. B.

Nephelometric Values of Cholesterol and the Higher Fatty Acids. FRANK A. CSONKA (*J. Biol. Chem.*, 1918, **34**, 577—582).—The nephelometric value of a substance is defined by the author as the turbidity produced by a given amount of the substance compared in a nephelometer with a given standard

within a given length of time. Taking oleic acid as a standard, for example, the nephelometric values of cholesterol, stearic and palmitic acids, are all different, but the nephelometric value of a mixture of any two of them is the sum of the nephelometric values of the constituents. The nephelometric value is influenced by the concentration of acid in the suspension, and the degree of turbidity changes with varying rapidity with the lapse of time. For every substance there is an optimum acid concentration which produces the highest nephelometric value with the least change within a specified interval of time.   H. W. B.

The Colloid Chemistry of Fehling's Sugar Test. M. H. FISCHER and M. O. HOOKER (*J. Lab. and Clin. Med.*, 1918, **3**, 368—373; from *Physiol. Abstr.*, 1918, **3**, 181).—The varying colours produced by Fehling's solution are ascribed to the different sizes of the reduced copper oxide particles held in suspension.

                                                        S. B. S.

Physiology of Blood-sugar. I. Bang's Micro-method of Sugar Estimation. RICHARD EGE (*Biochem. Zeitsch.*, 1918, **87**, 77—91).—A revision of Bang's method, directing attention more especially to the influence of the time taken in reduction on the results. The following suggestions are made: (1) A longer time than that suggested by Bang ("Methode zur Microbestimmung einiger Blutbestandtheile," 1916). (2) The use of a gas-regulator (figured in text). (3) Strict adherence to standard methods. Attention is also directed to a source of error from the fact that certain substances acting on iodine can be removed from the india-rubber of the apparatus. Methods for avoiding this source of error are indicated.   S. B. S.

The Microchemical Method of Estimation of Blood sugar. IVAR BANG (*Biochem. Zeitsch.*, 1918, **87**, 248—258).—The two chief errors in the author's method are due to differences in the intensity of boiling during the reduction, and to the oxidation by air during titration. The first of these can be overcome by passing the gas used for heating through a special form of valve, which is figured in the text, and the second by oxidising the reduced cuprous oxide by excess of potassium iodate and estimating the excess of iodate by titration. The solutions employed are the following: (1) Solution for coagulating the blood (weighed on filter paper by a torsion balance), 1360 c.c. of saturated solution of potassium chloride, 1·5 c.c. of 25% hydrochloric acid, 3 grams of uranyl acetate dissolved in 200 c.c. of water, and the mixture diluted to 2 litres. In this are dissolved 500 mg. of $CuSO_4,5H_2O$. (2) The iodate solution is made by dissolving 0·2230 gram of pure potassium iodate and 50 grams of potassium carbonate in 1 litre of water. (3) $N/100$- or $N/200$-thiosulphate solution. (4) 1% soluble starch, 2% potassium chloride solution. The weighed blood on the filter paper (about 0·1 gram) is extracted by 6·5 c.c. of

solution 1. The first extract is poured off, and a second extraction is made with 6·5 c.c. of the solution. Two c.c. of the iodate solution (No. 2) are then added, and the mixture is heated for exactly two minutes. Fifteen seconds before the end of this time, 2 c.c. of 20% (by volume) sulphuric acid are added. After cooling, potassium iodide solution (5%) is added, and titration is carried out by thiosulphate solution (No. 3), using starch (solution 4) as indicator. The difference between the result obtained and the titer of 2 c.c. of the original iodate solution gives the amount of sugar. 0·10 Mg. of dextrose is equivalent to 1·96 c.c. of $N/200$-thiosulphate solution. S. B. S.

The Microchemical Method of Estimating Dextrose. IVAR BANG and K. HATLEHOEL (*Biochem. Zeitsch.*, 1918, **87**, 264—272). —The authors find that exact timing of the heating for the reduction process in Bang's method (see preceding abstract) can be avoided by blowing a current of steam through the mixture for four minutes. A slight alteration must be made, however, in the solutions used, especially as regards the amounts of copper sulphate and alkali. The solution for extracting the filter paper containing the blood is as follows: 400 grams of potassium chloride, 3 grams of uranyl acetate, 1·5 c.c. of 25% hydrochloric acid, and 800 mg. of copper sulphate in 2 litres. The iodate solution contains 15 grams of potassium carbonate, 20 grams of potassium ammonium tartrate, and 0·3567 gram of potassium iodate in 1 litre. S. B. S.

A Modification of the Selivanov Reaction [for Detection of Ketoses or Sucrose]. F. WEEHUIZEN (*Rec. trav. chim.*, 1918, **37**, 302—303; *Pharm. Weekblad*, 1918, **55**, 831—832. Compare A., 1887, 459).—The reaction may be performed without heating the reacting mixture if a saturated solution of hydrogen chloride in absolute alcohol is used, and to it is added the mixture of sugars, under examination for the presence of a ketose or sucrose, and some resorcinol. A cherry-red coloration appears within three minutes. The method may be applied to the detection of sucrose in milk. [See, further, *J. Soc. Chem. Ind.*, 436A.] W. G.

Effect of Codeine in Hindering the Precipitation of Morphine by Ammonia from a Solution of its Lime Compound. H. E. ANNETT and HARDAYAL SINGH (*Analyst*, 1918, **43**, 205—213).—The Pharmacopœia method for the estimation of morphine in opium consists essentially in mixing the sample with calcium hydroxide and water, filtering the mixture, and precipitating the morphine in the filtrate in the presence of ether and alcohol. Codeine also dissolves in the calcium hydroxide solution, and its presence diminishes the quantity of morphine precipitated subsequently by ammonia, the effect increasing with the concentration of the solution and of codeine. The codeine may, however, be removed by extracting the solution with toluene previously to

the precipitation of the morphine, and this modification is recommended in the estimation of morphine in opium, particularly in Indian opiums with a high codeine content. Narcotine is quite insoluble in water in the presence of an excess of calcium hydroxide, either alone or mixed with morphine and codeine.   W P. S.

[**Estimation of Histidine in Proteins.**] WALTER E. THRUN and P. F. TROWBRIDGE (*J. Biol. Chem.*, 1918, **34**, 355—356).—See this vol., i, 324.

[**Estimation of Quinine in the Organism.**] HEINZ HARTMANN and LORO ZILA (*Arch. exp. Path. Pharm.*, 1918, **83**, 221—234).—See this vol., i, 328.

Is the Adamkiewicz Reaction due to Glyoxylic Acid or to Formaldehyde ? E. VOISENET (*Compt. rend.*, 1918, **166**, 789—792).—As opposed to the view of Hopkins and Cole (A., 1901, i, 310), the author considers that the colour reaction is due to the presence of formaldehyde and not of glyoxylic acid. A very dilute solution of formaldehyde readily gives the violet coloration in the presence of a trace of protein. The formaldehyde may be produced in the acetic acid by oxidation.   W. G.

Effect of Time of Digestion on the Hydrolysis of Casein in the Presence of Starch. J. S. McHARGUE (*J. Agric. Research*, 1918, **12**, 1—7).—The Van Slyke method for protein analysis, when applied to mixtures of casein and starch, in the proportion of 1 : 5, which have been hydrolysed from twelve to fifteen hours with 20% hydrochloric acid, gives results for the amino-acid groups that are comparable with those obtained by Van Slyke for casein alone. Prolonging the time of digestion with this strength of acid on such a casein–starch mixture brings about a redistribution of the nitrogen in the histidine and cystine groups. The insoluble residue from the casein–starch hydrolysis contains nitrogen, which is in an inert form and should not be included in the humin determination.   W. G.

Mechanical and Physical Analysis of Soils. G. RICHTER (*Int. Mitt. Bodenk*, 1916, **6**, 193, 318; from *Bied. Zentr.*, 1918, **47**, 49—52).—A discussion of the various methods for the mechanical and physical examination of soils; Kopecky's trituration method is preferred to that of Atterberg; Breitenbach's method for the estimation of the hygroscopic properties of soils gives higher results than those obtained by Mitscherlich's method. [See, further, *J. Soc. Chem. Ind.*, 384A.]   W. P. S.

General and Physical Chemistry.

The Scattering of Light in Hydrogen, Oxygen, and Nitrogen. M. Born (*Ber. Deut. physikal. Ges.*, 1918, **20**, 16—32). —In a previous paper (*ibid.*, 1917, **19**, 243), the author has shown that gases which consist of anisotropic molecules exhibit a scattering effect other than that which has been explained by Rayleigh's theory. The rays which characterise this new type of opalescence are in part non-polarised, and can accordingly be sharply distinguished from the polarised rays which are associated with the more familiar scattering effect. Experiments made by Smoluchowski on hydrogen, oxygen, and nitrogen afforded no evidence of the existence of the effect predicted by the author, and it is supposed that this may be due either to the insufficient anisotropy of the molecules or to the lack of precision in the method of observation.

By reference to the molecular models which have been recently suggested for hydrogen, oxygen, and nitrogen, the author has calculated the magnitude of the effects to be expected, and finds that, although small, it should be possible to observe the scattering effects in question in the case of each of these gases with a suitably designed arrangement of apparatus.   H. M. D.

Refractivities of Saturated and Unsaturated Compounds. GERVAISE LE BAS (*Trans. Faraday Soc.*, 1918, **13**, 414—419. Compare this vol., ii, 49).—From a comparison of the molecular refractivities of corresponding derivatives of benzene and of the saturated cyclic hydrocarbons, it is found that the augmentations due to substitution in the benzene ring are considerably greater than those which accompany substitution in rings of the polymethylene series. In this connexion, it may be noted that the unsubstituted saturated cyclic hydrocarbons show no anomaly in refractive power, whether the ring system is simple or complex.
H. M. D.

Ketonic and Enolic Modifications of Compounds. GERVAISE LE BAS (*Trans. Faraday Soc.*, 1918, **13**, 420—423).—The constitution of various keto-enol tautomerides is considered in relation to their refractivities. The molecular refractivities of acetylacetone, methylacetylacetone, ethyl oxaloacetate, ethyl mesityloxido-oxalate, methyl cyanoacetoacetate, ethyl acetylmalonate, ethyl acetonedicarboxylate, and ethyl β-hydroxy-α-phenylacrylate and its acetate lead to the conclusion that these substances exist in one form only, and that the different isomerides appear to be mutually exclusive.   H. M. D.

Presence in the Solar Spectrum of the Water Vapour Band λ 3064. A. FOWLER (*Proc. Roy. Soc.*, 1918, [*A*], **94,** 472—475). —A comparison is made of the lines composing the band λ 3064,

which is always obtained in the spectra of gases containing both hydrogen and oxygen, with the lines of the solar spectrum in this region as plotted and measured by Rowland. It is shown that, despite the interference of certain metallic lines, this band is also present in the solar spectrum.   J. F. S.

The Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum. A. FOWLER and C. C. L. GREGORY (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 470—471).—Photographs of the ammonia spectrum have been made by burning a copper arc in an atmosphere of ammonia. From these, it is shown that the ammonia spectrum consists of a main band, which is made up of a bright central maximum at λ 3360, a secondary maximum at λ 3371, and a number of lines, arranged in groups of three, which extend to a considerable distance in both directions. The lines composing the maxima are very closely crowded, and are found to be arranged in series of ordinary type. The components of the groups of three are widely separated near the central maximum, but the intervals rapidly diminish, and there is finally coalescence at λ 3450 towards the red and at λ 3287 towards the violet, where the lines fade out. This spectrum has been compared with the *P*-group of the solar spectrum, and shown to be practically identical; hence the presence of ammonia in the absorbing atmosphere of the sun is definitely established.   J. F. S.

The Ultra-red Absorption Spectrum of Water Vapour. GERHARD HETTNER (*Ann. Physik*, 1918, [iv], **55**, 476—496).— Measurements of the absorption of ultra-red rays by water vapour have been made for the region extending from the visible spectrum to a wave-length of 34 μ. An improved arrangement of apparatus for the investigation of absorption in the long-waved region is described. The results recorded show the existence of 78 maxima, of which only 20 have been recorded by previous observers. The wave-lengths of the maxima are tabulated, and a curve is given which shows the absorption relations in detail.   H. M. D.

Characteristic Ultra-red Vibrations of Nitrates. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1918, [iv], **55**, 577—588).—The reflection spectra of sodium nitrate, potassium nitrate, rubidium nitrate, lead nitrate, barium nitrate, and mercurous nitrate have been determined with polarised light and ordinary light. All six substances show three maxima, at approximately 7·5 μ, 12·5 μ, and 15·0 μ; in addition, mercurous nitrate shows a fourth maximum at 10·08 μ with ordinary light. From the examination with polarised light, it is shown for the biaxial nitrates that the three maxima observed with ordinary light are made up of three components corresponding respectively with the vibrations parallel to the axes of the three indices of refraction. The characteristic vibrations, as in the case of the carbonates and sulphates (A., 1916, ii, 506), depend very slightly on the

metal and are due to internal vibrations of the NO_3 group, which are practically the same in all the nitrates examined. The similarity between the space gratings of sodium nitrate and calcium carbonate, as put forward by Bragg, is discussed in the light of abnormalities found in the present work.   J. F. S.

The Distribution of Intensity in Series Spectra Excited by Cathode Rays. J. HOLTSMARK (*Ann. Physik*, 1918, [iv], **55**, 245—298).—The fact that previous attempts to measure the changes in the distribution of the intensity in series lines under the influence of varying conditions have not led to consistent results is attributed to errors introduced by the method of excitation. New experiments have been made on the Balmer series with cathode rays as the exciting agent, and the results indicate that the relative intensities of the series lines are, in these circumstances, independent of the current strength and also of the fall of potential. On the other hand, it is found that the lines of longer wave-length become relatively more intense as the pressure of the hydrogen increases. The connexion between the pressure p and the ratio K of the intensities of the lines H_β and H_γ is expressed by the equation $Kp^{-0.125} = $ constant. The pressure effect is not obtained when the increase of pressure is brought about by the addition of another gas to the hydrogen. Experiments in which the hydrogen was mixed with iodine, oxygen, argon, and helium respectively, all gave negative results in that these gases produced no change in the relative intensities of H_β and H_γ. On the other hand, observations made on the series lines of helium at different pressures showed a pressure effect similar to that found in the case of hydrogen.

The theoretical interpretation of the pressure effect is discussed, and the author concludes that Bohr's hypothesis relative to the origin of the effect is not in agreement with the observations.

H. M. D.

Electron Theory of the Natural Optical Rotatory Power of Isotropic and Anisotropic Liquids. M. BORN (*Ann. Physik*, 1918, [iv], **55**, 177—240).—A theoretical paper in which the author's previous attempts (compare A., 1915, ii, 659) to explain the natural rotatory power of optically active substances on a molecular basis in terms of electrons are more completely developed. The general formulæ derived are discussed in reference to the nature of the molecular forces and the symmetry relations, and are applied to the consideration of isotropic liquids with natural rotatory power, of liquids rendered anisotropic by means of an electric field, and of liquids which are normally anisotropic (liquid crystals).

H. M. D.

Colour Determination of Faint Luminescence. HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 439—449).—A method of determining the colour of faint luminescence is described which

consists in photographing the luminescence on a panchromatic plate and interposing a series of colour screens between the source of light and the plate. The method may be used in all cases when the glow is uniform and sufficiently strong to affect a highly sensitive photographic plate.

The results obtained in the investigation of the chemi-luminescence emitted in the oxidation of alkaline pyrogallol by hydrogen peroxide, of phosphorus in acetic acid solution by hydrogen peroxide, and of amarine in alkaline alcoholic solution by chlorine and bromine, are described in detail. The crystallo-luminescence emitted when a saturated aqueous solution of sodium chloride is mixed with alcohol or hydrochloric acid was also examined, with the result that the colour of the light is shown to be bluish-violet.   H. M. D.

Photolysis and Electrolysis. EMIL BAUR (*Helvetica Chim. Acta*, 1918, **1**, 186—201).—A theoretical paper in which the author evolves an electrolytic theory to explain the mechanism of photolysis. A substance which has been subjected to light has set up a molecular potential difference, and as such is capable of effecting a chemical reaction. Photolysis is therefore to be regarded as molecular electrolysis. Thus the decomposition of Eders's solution by eosin in light is to be regarded as a cathodic reduction of mercuric chloride to calomel and an anodic oxidation of oxalic acid to carbon dioxide, which may be expressed :

$$\text{Eosin}\begin{cases} \oplus + \tfrac{1}{2}C_2O_4{}'' = CO_2 \\ \ominus + HgCl_2 = HgCl + Cl' \end{cases}$$
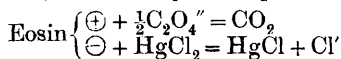
The author then proceeds to calculate the value of the *E.M.F.* operative on the basis of the quantum theory and the assumption that only one energy quantum may be absorbed. The following values are obtained for the lines mentioned: Sodium line, $\lambda = 589 \mu\mu$, $E = 2\cdot4$ volts; mercury line, $\lambda = 435 \mu\mu$, $E = 3\cdot2$ volts; Hg (fluorescent line), $\lambda = 253\cdot6 \mu\mu$, $E = 5\cdot5$ volts; and γ-rays, $\lambda = 0\cdot012 \mu\mu$, $E =$ about 100,000 volts. A large number of cases are considered in the light of this hypothesis.   J. F. S.

Absorption of *X*-Rays. E. A. OWEN (*Proc. Roy. Soc.*, 1918, [*A*], **94**, 510—524).—According to Bragg and Pierce (A., 1914, ii, 792), the atomic absorption coefficient A is connected with the atomic number N of the absorber, and the wave-length λ of the radiation by the equation $A = CN^4\lambda^{5/2}$, in which C is constant over considerable ranges of wave-length, but changes abruptly in the region of selective absorption. From the investigation of the absorption of a large number of aqueous solutions, Aurén (A., 1917, ii, 350) has recently deduced values for the atomic absorption coefficients of the elements which lead to the conclusion that with respect to the magnitude of the absorption coefficient, the elements may be divided into groups, for each of which the atomic absorption coefficient is directly proportional to the atomic number. An attempt is made to account for these discordant results.

The ordinary absorption coefficient is a composite quantity which represents the sum of the fluorescent absorption coefficient and the scattering coefficient. Assuming that the latter has a constant value equal to $0\cdot2$, in agreement with the results obtained by Barkla for the light elements and radiation of widely varying wave-length the author calculates from his observations the values of the atomic fluorescent absorption coefficient, and finds that this is nearly proportional to the fourth power of the atomic number of the absorber. Since it is known that the fluorescent absorption coefficient varies as the cube of the wave-length of the absorbed radiation, the connexion between the atomic fluorescent absorption coefficient A_f, the atomic number N, and the wave-length λ may be expressed in the form $A_f = CN^4\lambda^3$, where C remains constant over certain ranges of wave-length, but changes abruptly at critical points. This equation differs from that put forward by Bragg and Pierce in that the coefficient A_f is independent of the scattering of the radiation and refers only to the loss of energy of X-radiation resulting from the production of corpuscular radiations and the fluorescent X-radiations which accompany them.

The author's measurements were made on zinc, copper, nickel, iron, aluminium, magnesium, water, and filter-paper with radiation of wave-length $\lambda = 0\cdot586 \times 10^{-8}$ cm. (α-line of palladium), and the values obtained for the total absorption coefficients agree fairly closely with those recorded by Bragg and Pierce (*loc. cit.*).

It is further shown that, if the scattering coefficient is assumed to have a constant value of $0\cdot2$ for all elements from hydrogen to bromine, the equation $A_f = CN^4\lambda^3$ leads to values for the total absorption which are in close agreement with those obtained in the experiments of Aurén. H. M. D.

The Positive Ion as Carrier in the Canal Ray Fluorescence of Inorganic Salts. SVEN EM. OHLON (*Ber. Deut. physikal. Ges.*, 1918, **20**, 9—15).—When inorganic salts are subjected to the action of cathode rays of sufficiently high velocity, the salts fluoresce with the emission of the line spectrum of the metal present in the salt. For different salts of the same metal, the cathode ray energy required for this emissive effect increases with the heat of formation of the salt. The cathode ray energy at which emission begins is found to diminish as the discharge potential increases.

A similar series line emission occurs when inorganic salts are bombarded by canal rays, but the energy of the canal rays required to produce this effect varies to only a small extent when different salts of the same metal are employed, and the variation with magnitude of the discharge potential is also much smaller than in the case of cathode ray bombardment.

The observed differences suggest that the cause of the emission may not be the same in the two cases, and experiments have been devised with the object of elucidating further the changes which occur under the influence of canal rays. In these, the canal rays

were allowed to fall on the powdered salt contained in a small aluminium dish supported in the discharge tube in the path of the canal rays. The dish was connected through a galvanometer to earth, and a small direct-vision spectroscope was focussed on the bombarded salt. The discharge potential was varied, and by taking readings of the galvanometer, it has been found that the emission of the series lines is accompanied by a diminution in the positive current which flows through the galvanometer. This sudden change in the current, which characterises the transition from the non-fluorescent to the fluorescent condition, has been found to occur with salts of sodium, lithium. magnesium, calcium, strontium, barium, cadmium, and copper. The observations afford support for the view that the canal ray fluorescence is due to the metal ions which result from the dissociation of the salt under the influence of the canal rays. The carriers would thus appear to be the same for both cathode ray and canal ray fluorescence.

H. M. D.

Periods, Atomic Masses, and Electric Charges of the Radioelements. EMIL KOHLWEILER (*Zeitsch. physikal. Chem.*, 1918, **92**, 685—716).—A theoretical paper in which a number of regularities between the valency, average life, and ray emission of the radioactive elements are put forward. In each disintegration series, those elements which emit α-rays and have even valencies have longer average lives the greater the atomic mass. Of those pairs of elements which emit α-rays and have contiguous valencies (that is, IV, V), that with the smaller valency has the greater average life, whether the atomic mass of the pair is the same or not. Of two directly following β-ray changes, the first proceeds more slowly than the second, that is. the element with the smaller valency has the longer life. In the same disintegration series. elements which emit β-rays have longer lives the greater the atomic mass, whether the valency is odd or even. the odd and even valencies being considered separately. A similar rule holds for elements in the same group of the periodic system, but not in the same pleiad, with certain exceptions. There are very few exceptions to the above statements, and these occur generally in the least well investigated elements. The origin and atomic mass of actinium are discussed, and reasons are advanced for the value 226. The author also discusses the identity of isotopes and analogous radioactive elements, and finally the relationship of the radioactive elements to the periodic classification. J. F. S.

Ionisation of Gas during a Chemical Reaction. ALEXANDRE PINKUS (*Helvetica Chim. Acta*, 1918, **1**, 141—145; *J. Chim. Phys.*, 1918, **16**, 201—227).—With the object of ascertaining whether ionisation occurs during the interaction of two gases, the author has brought the following pairs of gases, (1) nitric oxide and oxygen, and (2) nitric oxide and chlorine, together in a large glass globe under a pressure of 0·25—0·5 atm. The walls of the

vessel were connected by iridioplatinum electrodes with a sensitive electrometer, and the rate of discharge was plotted. In the case of nitric oxide and oxygen, no formation of ions takes place, nor is there any evidence that ionisation occurs during the reaction between chlorine and nitric oxide if the chlorine is not in excess. Should the chlorine be in excess, there is a marked ionisation. The author attributes the ionisation to the intermediate formation of $NOCl_2$.   J. F. S.

Resonance and Ionisation Potentials for Electrons in Sodium Vapour. JOHN T. TATE and PAUL D. FOOTE (*J. Washington Acad. Sci.*, 1918, **7**, 517—525).—In the further investigation of the potentials at which electrons give rise to the emission of rays, experiments have been made on sodium vapour The resonance potential at which rays corresponding with the *D*-lines are emitted is found to be $2\cdot12 \pm 0\cdot06$ volts, the value calculated on the basis of Bohr's theory being $2\cdot10$ volts. When the potential reaches $5\cdot13 \pm 0\cdot1$ volts, ionisation of the sodium vapour occurs. This is identical with the value calculated on the basis of Bohr's theory by using the limiting wave-length of the principal series of lines in the sodium spectrum.

The lower potentials found by Wood and Okano (*Phil. Mag.*, 1917, [vi], **34**, 177) in their observations on the emission of the *D*-lines by sodium vapour suggest that ionisation of the vapour occurs under the influence of more slowly moving electrons. A full account of this and the previous paper (A., 1918, ii, 94) is to be found in *Phil. Mag.*, 1918. [vi], **36**, 64—75.   H. M. D.

Relation of the Electrical Conductivity to the Periodic System of the Elements. E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, **20**, 53—62).—According to Benedicks (*Jahrb. Radioaktiv. Elektronik.*, 1916, **13**, 351), the atomic conductance, measured by the product of the specific conductance and the atomic volume, is a periodic function of the atomic weight. The conductance data used by Benedicks are not strictly comparable, however, for the influence of temperature is by no means the same for the different elements. It is suggested that conductance data for corresponding temperatures should be used in the comparison of the atomic conductances, and in accordance with the empirical formula referred to in the following abstract, such temperatures are those which bear the same ratio to the characteristic temperatures.

By reference to the data which are available for this comparison, it is shown that the atomic conductance is a periodic function of the atomic weight, and that the value decreases from the first to the eighth group in the periodic table.   H. M. D.

Electrical Conduction of Metals at Low Temperature. E. GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1918, **20**, 36—52. Compare A., 1913, ii, 377).—By reference to the data for lead,

cadmium, zinc, mercury, gold, platinum, silver, and copper, the author has tested the empirical formula $w \sim T \cdot F(T/\Theta) \cdot C_p/C_v$ for the influence of temperature on the electrical resistance of metals. In this formula, w represents the resistance, T the absolute temperature, $F(T/\Theta)$ a universal function of T/Θ, where Θ is the characteristic temperature of the metal according to Debye's theory. It is shown that the formula affords a satisfactory account of the observed variations in the conductivity of metals over a wide range of temperature, and the author infers that the empirical expression affords a close approximation to the statement of the actual law which connects conductivity and temperature.   H. M. D.

Electronic Theory of the Metals. Th. Wereide (*Ann. Physik*, 1918, [iv], **55**, 589—607).—A theoretical paper in which the electronic theory of metals is discussed. It is shown that, apart from a numerical correction, Drude's formula for electric conductivity is unassailable. The formula $x = \frac{1}{2} \cdot e^2/m \cdot nl/v$ has been modified by eliminating the three unknown, n, l, and v, and in their place introducing the three atomic constants v=vibration number of an atom, ϵ=emission number of an atom, and a=absorption coefficient of an atom. The constant a bears the relationship $a = ca$ to Lenard's coefficient a, where c is the number of atoms per c.c. The Lenard theory gives then the formula $x = e^2\epsilon/6ca^2 \cdot (e^{hv/kT} - 1)hv$ for the electric conductivity and a similar formula for thermal conductivity. On the basis of this formula, the reasons for the following points are explained. (1) At high temperatures, the electric resistance is approximately proportional to the absolute temperature. (2) The change in resistance depends on the energy change of the substance. (3) The resistance approaches zero at the absolute zero. (4) The conductivity curve and the atomic volume curves have a similar form. (5) Under similar conditions, the conductivity is greater the greater the electro-affinity of the atoms.   J. F. S.

Calculation of the Position of the Conductivity Minimum in Neutralisation. W. D. Treadwell (*Helvetica Chim. Acta*, 1918, **1**, 97—110).—The author has calculated the position of the conductivity minimum in the neutralisation of (1) a diluted strong acid by a diluted strong base, (2) a weak monobasic acid by a diluted mono-acidic strong base, (3) a mixture of two weak monobasic acids of different strengths by a strong mono-acidic base, and (4) a mixture of a monobasic weak acid and a monobasic strong acid by a strong mono-acidic base. In the first case, the minimum of conductivity lies exactly at the point of neutralisation; in the second case, using equal concentrations of acetic acid and alkali, the minimum occurs when there is an excess of 0.4% of acid present, or generally if x represents the number of c.c. of alkali of concentration c_2 which is present to 1 c.c. of acid of concentration c_1, then $x = c_1/c_2 \times k_1/k_1 + \sqrt{k} \cdot l_{OH}/l_H$. The influence of decreasing

strength and concentration of the acid on the position of the minimum is also calculated. The conductivity minimum is calculated in the case of a number of acids, and these values are compared with the experimental values of Thiel and Roemer. Good agreement is found between the two sets of values.   J. F. S.

Calculation of the Electrochemical Normal Potential.

KARL F. HERZFELD (*Ann. Physik*, 1918, [iv], **56**, 133—160).—A mathematical paper in which the normal potential of the ions is calculated on the assumption that the entropy constant of the dissolved ions is the same as that of the corresponding atoms. The numerical results of this calculation differ from the experimental values, but the amount of divergence is the same for ions of equal mobility. The divergences are therefore attributed to complex formation of the ions with water. From these calculations, formulæ for the solubility of salts are deduced. In open cells, only the positive ions are in equilibrium, for the electrons only slowly reach equilibrium; hence the cell at first only approximates to a reversible element. In this connexion, the mechanism of the semi-permeable membrane is discussed. Calculations are made for metals of the single potential, the contact potential, and the electron number. The Helmholtz equation is not strictly applicable to single electrodes.   J. F. S.

[Potentials due to the Flow of Electrolytes through Capillary Tubes and the Stability of Colloids.]   H. R.

KRUYT (*Kolloid Zeitsch.*, 1918, **22**, 81—98).—The potential differences produced by the flow of solutions of electrolytes through a capillary tube have been measured in experiments with solutions of different chlorides. In the apparatus used, the capillary tube formed part of the connexion between two glass vessels fitted with silver electrodes coated with silver chloride, and the chloride solution was made to pass through the glass capillary from one vessel to the other under the influence of a constant pressure difference.

The results obtained with solutions of potassium, barium, and aluminium chloride show that the influence of the cation on the potential difference between the electrodes depends very largely on the valency of the cation. The relations are in general very similar to those which were found by Powis (A., 1915, ii, 137) in the investigation of the influence of the three chlorides on the cataphoresis of hydrocarbon oil emulsions. In both series of observations, the effects are attributable to the adsorption of electrolytes. The author's experiments seem to show, however, that in very dilute solutions the contact potential is increased by the presence of the electrolyte. It is probable that this fact explains the well-known peptonising action of electrolytes in very dilute solution and the essential importance of small quantities of electrolytes in connexion with the stability of colloidal systems.

H. M. D.

15*

Passivity of Chromium. II. A. H. W. ATEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1119—1134. Compare this vol., ii, 183).—In the further investigation of the electrochemical behaviour of chromium, measurements have been made of the potential of chromium when subjected to anodic and cathodic polarisation.

The phenomena associated with the anodic polarisation of electrolytic chromium depend to some extent on the nature of the metal on which the chromium has been deposited. If the metal immersed in a solution of chromous sulphate is anodically polarised with a sufficiently strong current, the chromium becomes passive, but when the current is interrupted, the potential of the metal is found to be more negative than before polarisation. The passivation during anodic polarisation and activation after this treatment are shown by chromium which has been deposited on copper, silver, or gold. The degree of activation after anodic polarisation increases with the strength of the polarising current.

Chromium, prepared by Goldschmidt's process, which has been activated by treatment with molten zinc chloride, or a mixture of sodium and potassium chlorides, may be anodically polarised in a solution of potassium chloride without becoming passive. The resistance offered by the metal to the action of the polarising current is greater when the strength of the current is gradually increased than when the current strength is increased rapidly. The resisting power of the metal is smaller when the chromium has been previously subjected to cathodic polarisation. If the chromium has been rendered passive by anodic polarisation in a solution of potassium chloride, the active condition may be restored by heating the solution. This change occurs even when the polarising current is continued during the heating of the solution and, on cooling, the chromium remains in the active condition provided that the current is not too strong.   H. M. D.

Allotropy of Cadmium. VI. ERNST COHEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1177—1185).—A criticism of the conclusions drawn by Getman from his observations (compare A., 1917, ii, 533) on the *E.M.F.* of Cd|CdSO$_4$|Cd amalgam cells. According to Getman, the influence of temperature on the *E.M.F.* of cells containing 8% cadmium amalgam points to the existence of two allotropic forms of cadmium with a transition point at 37·5°. The discontinuity in the temperature coefficient of the *E.M.F.* at this temperature is, however, to be attributed to a change in the amalgam at this temperature. According to Bijl's investigations (A., 1903, ii, 6), the 8% amalgam used by Getman undergoes transformation at about 40°, and the resulting change in the electromotive behaviour of the amalgam has been erroneously attributed by Getman to the transformation Cd-α into Cd-β. The actual results obtained by Getman are considered to afford confirmation of the views which have been previously put forward

by the author as a result of his investigation of the allotropy of cadmium (A., 1914, ii, 52, 652; 1915, ii, 40, 144).   H. M. D.

Magnetic Susceptibility and Electric Resistivity. F. H. LORING (*Chem. News*, 1918, **117**, 229—231).—A theoretical discussion of magnetic susceptibility in which the author assumes that ferro-, para-, and dia-magnetic qualities are to be explained in terms of atomic and molecular currents which are dependent on the specific resistances of the elements concerned.   H. M. D.

The Influence of the Finite Volume of Molecules on the Equation of State. MEGH NAD SHAHA and SATYENDRA NATH BASU (*Phil. Mag.*, 1918, [vi], **36**, 199—202).—Starting from Boltzmann's entropy principle, the authors have obtained a new equation of state which may be written in the form $pV = NK\theta x/1 - e^{-x}$, where $x = \beta p/K\theta$. In these equations, K represents Boltzmann's gas constant, N the number of molecules contained in volume V, θ the temperature, and $\beta = 8 \times$ volume of a single molecule. From this equation of state, the critical volume $V_c = 3 \cdot 166b$ and $K = 3 \cdot 513$. The values of V_c derived from the van der Waals and Dieterici equations are $3b$ and $2b$ respectively, and the values of K $2 \cdot 66$ and $3 \cdot 695$ respectively.   H. M. D.

The Course of the Values of a and b for Hydrogen at different Temperatures and Volumes. II. J. J. VAN LAAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1195—1212. Compare this vol., ii, 185).—A theoretical paper in which the pressure–volume relations are further discussed in reference to the variability of a and b.   H. M. D.

Isothermals of Monatomic Substances and their Binary Mixtures. XIX. Vapour Pressures of Neon between the Boiling Point and the Critical Point. P. G. CATH and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1160—1162).—The vapour pressures of liquid neon have been measured at temperatures ranging from $24 \cdot 42°$ to $44 \cdot 43°$ (abs.). The results are satisfactorily reproduced by the formula $T \log p = -65 \cdot 061 + 2 \cdot 8191T + 0 \cdot 01118T^2$, where p denotes the vapour pressure in atmospheres.

A comparison of the reduced vapour pressure curves for oxygen, nitrogen, argon, neon, and hydrogen has been made, and from this it appears that the divergence between hydrogen and neon is much greater than that between neon and argon, in spite of the fact that the critical temperature of neon is relatively low.

H. M. D.

The Characteristic Equation of Fluids. PIERRE WEISS (*Compt. rend.*, 1918, **167**, 232—235. Compare *ibid.*, 1918, **167**, 78).—The isochores for air, ethylene, ether, and isopentane are

given, and in each case they consist of rays of straight lines each showing one point of inflection. They resemble the magnetic isotherms (*loc. cit.*).   W. G.

The Entropy of a Metal. H. Stanley Allen (*Proc. Physical Soc. London.* 1918, **30**, 215—220).—The formula derived by Ratnowsky (*Ber. Deut. physikal. Ges.*, 1914, **16**, 1033) for the entropy of a substance in the solid state is found to give values for a number of metals in very close agreement with those recorded by Lewis and Gibson (this vol., ii, 29). The assumptions made by Ratnowsky in deducing his entropy formula are examined, and the conclusion is drawn that these are justified as being at least approximately true.   H. M. D.

Boundaries of Existence of the Liquid State. Julius Meyer (*Zeitsch. Elektrochem.*, 1918, **24**, 138—139 Compare Herz, this vol., ii, 150).—A criticism of Herz's definition of the boundaries of the liquid state. Herz makes the melting point and the critical point the limits of existence of a liquid, whereas Meyer is of opinion that no such points can be specified.   J. F. S.

Boundaries of Existence of the Liquid State. W. Herz (*Zeitsch. Elektrochem.*, 1918, **24**, 139. Compare preceding abstract).—Polemical; an answer to Meyer (*loc. cit.*).   J. F. S.

Boiling Points of the Paraffins. Gervaise Le Bas (*Chem. News*, 1918, **117**, 241—242).—A theoretical paper in which it is shown that the rule of Hinrichs and Naumann, which states that the more the chain of a molecule is branched the lower will be the boiling point, is not generally to be followed. It is shown that the boiling point depends on whether the hydrogen attached to the β-, γ-, δ-, etc., carbon atoms has been displaced by methyl groups. In dealing with this question, it is necessary to consider the formulæ of *iso*-compounds. It is the practice of writing the formula of an *iso*-compound thus, $\overset{Me}{\underset{Me}{>}}CHR$, which tacitly assumes that it consists of two similar methyl groups attached to one carbon atom. From the point of view of the boiling points, this is not true. This class of structure involves the displacement of an hydrogen atom attached to the α-, β-, γ-, δ-, etc., carbon atom of the hydrocarbon by a single methyl group. The difference in boiling point due to this structure is 6° or 7° when substitution of a β-methylene group has been effected, and slightly more, 9°, when the γ-methylene group has been substituted.   J. F. S.

Method for the Determination of the Relation between Vapour Pressures and their Corresponding Temperatures at Pressures of less than Five Millimetres. W. R. Ham, J. C. Churchill, and H. M. Ryder (*J. Franklin Inst.*, 1918, **186**, 15—28).—The substance under investigation is subjected to slow distillation and condensation in a closed system of considerable

capacity, the pressure in which is reduced to a low value determined with the aid of a McLeod gauge which is attached to the closed system. The system is also connected with a reservoir of pure dry hydrogen, the object of this arrangement being to ensure accuracy in the readings of the McLeod gauge. The pressure in the apparatus is varied by running the pump at different speeds, the driving motor being suitably controlled. The liquid in the distilling flask is electrically heated by passing a current through a platinum wire immersed in the liquid, and the vapour evolved passes through a side-tube, in which a thermometer is supported, to a condenser, from which the condensate drops into a receiver. For a given rate of working of the pump, a series of observations is made in which the liquid is distilled at different rates determined by the number of drops of liquid which fall from the end of the condenser tap into the receiver in a fixed interval of time. In each of these experiments, the temperature of the vapour registered by the thermometer is recorded. By plotting the temperature against the rate of distillation, a smooth curve is obtained, and by extrapolation to zero rate of distillation, a temperature is obtained which corresponds with the pressure in the closed system as measured by the McLeod gauge.

Results obtained for acetophenone by this method show close agreement with the values obtained for this substance by Kahlbaum, who measured the depression of a barometric column. The results may be expressed by the equation $\log P = 19 \cdot 696 - 72 \cdot 540 \times 0 \cdot 993944^T$, or by the equation $\log P = 16 \cdot 152 - 3390 \cdot 96/T - 534192 \cdot 38/T^2$.   H. M. D.

The Solutions of Gases in Liquids. Félix Michaud (*Ann. Physique*, 1918, [ix], **9**, 203—232, 233—258. Compare A., 1917, ii, 122).—A theoretical discussion of the subject. Contrary to Duhem's conclusions, the presence of a gas in solution at constant temperature does not always lower the vapour pressure of the solvent. That only occurs if the pressure of the solution is maintained constant by means of an auxiliary, insoluble gas. It is possible to obtain a simple formula from which the vapour pressure of the solvent can be calculated in terms of the pressure of the gas, the formula being really an expression of Raoult's law for a very soluble, normal gas which obeys Henry's law. A cryometric study of solutions of gases leads to similar results.

From a study of the calorific phenomena which accompany the solution of a gas, a simple expression for the entropy of reversible solution can be obtained. A formula is also established connecting the specific heat of a solution of a gas in a liquid with the coefficient of solubility of the gas.   W. G.

Iso-piestic Solutions. W. R. Bousfield (*Trans. Faraday Soc.*, 1918, **13**, 401—410).—Solutions of various salts were placed in an exhausted desiccator and allowed to remain at constant temperature until the several solutions were in equilibrium with

one another. The resulting solutions have the same vapour pressure at the temperature of the experiments, and are termed iso-piestic.

Results obtained at 18° show that iso-piestic solutions of potassium chloride, sodium chloride, and lithium chloride contain different numbers of molecules of water per molecule of salt. The value of this molecular ratio (h) for a saturated solution of potassium chloride is 12·41, whilst for the iso-piestic solutions of sodium chloride and lithium chloride $h = 14·16$ and 17·07 respectively. Although the total quantities of water thus differ appreciably for the three salts, it is calculated that the quantities of uncombined water are very nearly the same. The differences in h are due to differences in the quantities of combined water, for which the respective molecular ratios are approximately 1, 3, and 6.

Observations in which the dry salts were exposed to the action of water vapour at different pressures lead the author to the conclusion that for substances which do not form crystalline hydrates there is, at a given temperature, a certain pressure of aqueous vapour below which the dry substance will not take up water vapour, and if the substance is not dry originally, it will become so provided the pressure of aqueous vapour is lower than this critical value, which is called the critical hydration pressure of the substance.   H. M. D.

Measurement of Very Low Temperatures. XXVII. Vapour Pressures of Hydrogen in the Neighbourhood of the Boiling Point and between the Boiling Point and the Critical Temperature. P. G. CATH and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1155—1159).—The vapour pressures of liquid hydrogen have been determined at temperatures between 24·59° and 32·93° (abs.). The results obtained are satisfactorily represented by the formula $T \log p = -56·605 + 3·8015T - 0·10458T^2 + 0·003321T^3 - 0·00005102T^4$, in which p represents the pressure in international atmospheres. Further measurements of the vapour pressure in the neighbourhood of the boiling point have given for this 20·39° (abs.). This value is 0·04° lower than the value obtained in a previous series of measurements.   H. M. D.

The Saturated Vapour Pressures of Octa-atomic Substances. E. ARIÈS (*Compt. rend.*, 1918, **167**, 118—122).—The formula derived for the saturated vapour pressures of octa-atomic compounds is $\Pi = \tau^{29/10} Z / x$, where

$$x = [1 + (1 - \tau)(0·88 - \tau) / \{0·8 + (1 - \tau)^2\}]\tau^{19/10}.$$

The values, observed and calculated, are in fairly close agreement in the cases of methyl formate, ethyl bromide, and ethyl chloride, but in the cases of acetic acid and ethane it is not possible to obtain satisfactory verifications.   W. G.

Ebullioscopic Determinations with a Common Thermometer. C. C. KIPLINGER (*J. Amer. Chem. Soc.*, 1918, **40**, 1020—1023).—An arrangement is described whereby an ordinary

thermometer having a solid stem graduated in degrees may be read to hundredths of a degree with an error not exceeding 1%. A meter rod graduated in mm. is attached to a stand and equipped with a sliding peep-sight made from a strip of thin sheet metal. This rod is set parallel with the thermometer, the hole of the peep-sight being at a distance of 6 inches from the thermometer scale. The thermometer is fitted with a pen-shaped metallic indicator tapered to a width at the point equal to the apparent width of the capillary. The indicator is blackened, bent so that the tip is at a distance of 3 mm. from the scale, and attached to the thermometer by a screw clamp. The position of the mercury meniscus with reference to the nearest scale division is determined as follows. For clearness of explanation, let the meniscus be denoted by the letter P, the nearest scale division by D, and the tip of the indicator by A. Light is projected by a mirror on to the meniscus. The sliding peep-sight is moved until the scale division D is just hidden behind the tip A of the indicator; if the position of the peep-sight on the rod is denoted by X, then XAD is a straight line. The peep-sight is then moved to a position Y in which the gleam of the meniscus P is just hidden behind the tip A. The position of the meniscus P with reference to D is thus determined by the angle XAY; the distance XY once known, the apparatus may be dismantled, set up again, and the position of P with reference to D as definitely fixed as before, provided the indicator has not been moved relatively to the scale mark D.

In using the apparatus to determine molecular weights ebullioscopically, the principle adopted is to vary the concentration of the solute under examination until the rise of the b. p. is exactly the same as that produced by a substance of known molecular weight. For example, about 30 grams of carbon tetrachloride (constant 48) are placed in the weighed boiling tube with a known amount of borneol. When the temperature has become constant, the angle XAY, expressed in terms of divisions of the mm. scale, is determined as above, thus establishing the point P. The barometer is read, and the tube and its contents are weighed to determine the true weight of the solvent. Knowing the weight of the solvent and of the solute, and the molecular weight of the latter, the rise of the b. p. is calculated. The apparatus is cleaned and weighed, and a weighed amount of the substance of unknown molecular weight is added, together with a few grams of solvent. The solution is brought to the b. p., and small portions of solvent are added from time to time until the meniscus reaches the same point as in the borneol trial, as determined by the angle XAY. If too much solvent has been added, the condenser may be detached to allow some of the solvent to evaporate. When the adjustment is correct, the tube and its contents are weighed to ascertain the weight of the solvent. The rise of the b. p. is known from the borneol trial, hence the molecular weight can be calculated. In both cases, the same point D on the thermometer has been used

for reference, hence a calibrated thermometer is unnecessary. The height of the flame must be kept constant throughout the work.

Molecular weights (the average of a series of determinations) determined in this manner compare favourably with those obtained by the usual method.   C. S.

A Laboratory Apparatus for Distilling in [Superheated] Steam under Reduced Pressure. C. HARRIES and REINOLD HAARMANN (*Ber.*, 1918, **51**, 788—790).—Steam at 3—4 atmos. pressure is admitted through a throttle-valve into a superheating chamber maintained at about 300°, and then into the substance in the exhausted distilling flask, the neck of which is filled, by a simple device, with small pieces of glass rod in order to break up froth and prevent spirting. The apparatus is completely described with illustrations, and it is claimed that substances otherwise very non-volatile can be purified easily by distillation in this way, and hygroscopic salts deprived of solvent water.   J. C. W.

Definitions of Explosive Substance, Explosive Action, and Thermite. HANS SCHIMANK (*Zeitsch. Elektrochem.*, 1918, **24**, 213—214).—An explosive substance is defined as a substance which undergoes a very rapid exothermic change with the formation of gaseous products. Explosive action is differentiated from such actions as occur in overheated steam boilers. Thermite is a system which is capable of undergoing rapid exothermic reaction without the formation of gaseous products.   J. F. S.

Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements. KARL FEHRLE (*Physikal. Zeitsch.*, 1918, **19**, 281—286).—A theoretical paper in which the author derives an expression for the heat of formation of a compound which involves only the atomic weights of the reacting elements and the densities of the elements and the compound formed.   H. M. D.

Thermal Properties of Sulphuric Acid and Oleum. ALFRED W. PORTER (*Trans. Faraday Soc.*, 1918, **13**, 373—399).— The thermal data bearing on the concentration of sulphuric acid by evaporation have not hitherto been determined by experiment, and in view of the technical importance of the quantities in question, the author has attempted to supply the requisite information by indirect methods involving thermodynamical relations. The thermal data for the ordinary temperature are utilised in conjunction with calculations which give the variation of the heats of solution and dilution with temperature, and from these results the heats of total evaporation of water from sulphuric acid solutions at different temperatures are derived. A method of graphical representation, which facilitates the determination of the thermal data which may be required in a particular case, is described.

In the second part of the paper, similar methods are employed

in the calculation of the thermal data for oleum (fuming sulphuric acid), and in particular of the heats of total evaporation or condensation of sulphur trioxide vapour for sulphuric acids containing 80—90% of sulphur trioxide. H. M. D.

Experimental Determination of the Fictitious Heat of Solution. ERNST COHEN and H. R. BRUINS (*Zeitsch. physikal. Chem.*, 1918, **93**, 43—58).—By the term fictitious heat of solution is to be understood the heat change which occurs when 1 gram-molecule of a substance at a measured temperature and pressure dissolves in an unlimited amount of its own saturated solution at the same temperature and pressure. Four methods of determining this value are described, and of these two have been used to determine the value for cadmium iodide in water. To measure the fictitious heat of solution of a salt KA, two galvanic elements, XY, are connected so as to oppose one another, and the resulting $E.M.F.$ is measured.

X.			Y.		
Electrode reversible with respect to K.	Saturated solution of KA without solid phase.	Electrode reversible with respect to A.	Electrode reversible with respect to A.	Very dilute solution of KA.	Electrode reversible with respect to K.

According to the Gibbs-Helmholtz equation, $E_c = n\epsilon(E_e - T \cdot dE/dT)0\cdot2389$ gram cal., where E_e is the $E.M.F.$ and E_c the chemical energy of the double cell; also $E_c = W - F$, where F is the fictitious heat of solution and W the heat of solution of the dilute solution of KA. Consequently, $F = W - n\epsilon(E_e - T \cdot dE/dT)$ gives the value of F.

In the second method, the combination

Electrode reversible with respect to K.	Saturated solution of KA without solid phase.	Dilute solution of KA.	Electrode reversible with respect to K

is measured, and from the equation $F = W - n/n_1 \cdot \epsilon(E_e - T \cdot dE/dT)0\cdot2389$ gram cal., the heat of solution is obtained; the symbols have the same meaning as before; n_1 is the number of gram ions transported from the saturated solution to the dilute solution by the passage of $\epsilon = 96,494$ coulombs. This method is complicated by the contact potential existing at the boundary of the two solutions.

The third method consists in measuring the $E.M.F.$ and temperature coefficient of the cell X and of the same cell with solid phase X_1, and then using the equation of the same kind as those given above, the value of F follows. A series of $E.M.F.$ determinations of these cells has been made at 16°, 18°, 20°, 22°, and 24°, and the temperature coefficient calculated for the case of cadmium iodide and the value -1246 gram cal. determined at 18°.

The fourth method depends on the measurements made in the last method; the relationship
$$(dE/dT)_X^1 = (dE/dT)_{X1} + (dE/dC)_T \cdot (dC/dT)$$

exists between the temperature coefficients of X and X_1; dC/dT is the temperature coefficient of the solubility, by substitution $F = [T . (dE/dC)_T . (dC/dT)]46,105$ gram cal. Hence to determine F, the values of $(dE/dC)_T$ and (dC/dT) have to be determined.

These measurements have been made for cadmium iodide; the solubility of cadmium iodide is expressed by the equation $C = 44.18 + 0.0828t + 0.000183t^2$, consequently $(dC/dT)_{18} = +0.08939$. To ascertain the value of dE/dC, the $E.M.F.$ of a number of elements $Cd/CdI_2 \parallel$ of different concentrations have been measured at 18°, whence the dependence of the $E.M.F.$ on concentration is given by the equation $E_{18} = 0.43150 + 0.000283C - 0.00001428C^2$, so that $(dE/dC)_{18} = -0.001023$ volt per cent. Using these values, $F = -1227$ gram cal. at 18°.   J. F. S.

Relative Volume Change which occurs on Mixing two Chemically Indifferent Gases, and its Measurement by Refraction of Light.
PAUL FUCHS (*Zeitsch. physikal. Chem.*, 1819, **92**, 641—676).—The change in total volume on mixing two chemically indifferent gases has been determined over the whole range of mixtures for the pairs nitrous oxide–nitrogen, carbon dioxide–nitrogen, oxygen–nitrogen, nitrous oxide–carbon dioxide, nitrous oxide–oxygen, oxygen–carbon dioxide by means of refraction measurements. The Haber-Löwe interferometer was used for this purpose, and the measurements were made at ordinary temperature and pressure. In every case, there is an increase in volume on mixing which is greater the more the two components differ in their physical behaviour. The volume change does not correspond with the ratio in which the gases are mixed, but reaches a maximum at a point beyond the equal concentration point in the sense that the maximum change lies with mixtures containing more than 50% of the gas of smaller critical temperature. The maximum volume change lies nearer to the 1:1 mixture the more the components resemble one another. The van der Waals's expression, $\Delta v = x(1 - x)[\{a_1 + a_2 - 2a_1a_2\}/MRT - \{b_1 + b_2 - 2b_1b_2\}]$, was tested by means of the data obtained and found to be qualitatively in accord with the general results, but not strictly quantitatively correct. The dispersion of the gaseous mixtures is markedly different from that of the sum of the two components.
                                                            J. F. S.

The Vapour Pressure of Dissociating Substances and the Volatilisation of Ammonia.
RUD. WEGSCHEIDER (*Zeitsch. anorg. Chem.*, 1918, **103**, 207—220).—An expression has been evolved for calculating the vapour pressure curves of dissociating substances, particularly those which on volatilisation dissociate partly into two molecules. The data required for the calculation are: the specific heats of solid (or liquid) and of dissociated and undissociated vapour; the heat of evaporation without dissociation and the heat of dissociation for each temperature; the dis-

sociation constant and the vapour pressure for one temperature. The expression is used to examine the probability of different explanations put forward to account for the two vapour pressure curves of ammonium chloride. This substance is dimorphous, with a transition point at 184·5°, but the dimorphism will not account for the form of the curves unless the heat of transformation is at least -3000 cal., whereas the observed value is only -1030 cal. The assumption of further polymorphism with a second transition point either above or below 184·5° is shown to be invalid. The possibility is not excluded, however, that the ordinary form of ammonium chloride is labile, changing into the stable form only at high temperatures in presence of moisture. When perfectly dry, this labile form volatilises without dissociation, and its vapour pressure must be greater than the partial pressure of the undissociated molecules in the vapour of the stable form. An alternative explanation of the contradictory results sometimes obtained is that, whilst the ordinary form of ammonium chloride is stable, at times a labile form is obtained which when dry volatilises unchanged.   E. H. R.

The Principles of Diffusion, their Analogies and Applications. HORACE T. BROWN (T., 1918, **113**, 559—585).—A lecture delivered before the Chemical Society on June 6th, 1918.
                                                                D. F. T.

Condition of Double Salts in Aqueous Solution. D. MERRILL TORRANCE and NICHOLAS KNIGHT (*Chem. News*, 1918, **117**, 270—272. Compare Maxwell, A., 1917, ii, 562).—The changes, occurring in the diffusion of solutions prepared from sodium aluminium sulphate, copper potassium sulphate, copper ammonium sulphate, magnesium ammonium sulphate, and potassium chromium sulphate have been examined at different temperatures and at different concentrations. The results indicate that the double salts are largely dissociated into the respective simple salts. The relative rates of diffusion appear to be influenced appreciably by ionic hydration.   H. M. D.

Hydrogen Ion and Hydrogen Bound to Ionogens: Chemistry of Electrolytic Dissociation. A. HANTZSCH (*Zeitsch. Elektrochem.*, 1918, **24**, 201—213).—A theoretical paper in which the intramolecular change involved in the formation of pseudo-acids is discussed. In this connexion, the position and method of linking of the hydrogen atom are considered, and theories put forward to explain the behaviour of the hydrogen in the different positions. The author proposes to substitute for the optical method of determining constitution the action of the substance in question on diazo-esters. The pseudo-acid is without action on the diazo-ester, whereas the true acid liberates nitrogen freely. A modification of the processes generally held to be occurring in ionisation is discussed.   J. F. S.

Liquid Crystals. TARINI CHARAN CHAUDHARI (*Chem. News,* 1918, **117**, 269—270).—For closely related compounds, the intervals of temperature over which the liquid crystalline phase is stable appear to be simply related. Smits's dynamic theory of polymorphism in its application to liquid crystalline forms is considered to be unsatisfactory. There appears to be no definite connexion between the constitution of compounds and their capacity to form liquid crystals, and the author advances the view that the formation of such crystals is a general property of organic substances which melt without decomposition. H. M. D.

Non-molecular Structure of Solids. ARTHUR H. COMPTON (*J. Franklin Inst.,* 1918, **185**, 745—774).—The fact that the X-ray examination of certain simple crystals has shown that these have a non-molecular structure, suggests that this may be characteristic of all solid substances. In support of this hypothesis, a number of arguments are put forward, and the conclusion is drawn that in the solid state of aggregation the atoms are so intimately intermingled that particular molecules cannot be said to have any real existence.

The dependence of crystal form on chemical composition, X-ray observations, and considerations relative to the law of Dulong and Petit and the nature of cohesion, all suggest that the atoms of a crystalline solid oscillate about a mean position of stable equilibrium, and a comparison of the nature of cohesive forces with those which are concerned in chemical combination indicates that these are of the same nature and of the same order of magnitude. In this connexion, it is pointed out that there is a close parallelism between the melting temperatures and the "atomic heats of formation" for a large number of different substances. The melting point may be supposed to afford an approximate measure of the firmness with which the molecules are held together in the solid substance, whilst the "atomic heat of formation," obtained by dividing the molecular heat of formation by the number of atoms in the molecule, may be supposed to measure the intensity of the intramolecular forces.

Although certain properties of solid matter have been explained on the assumption that the ultimate atoms are definitely grouped into molecules, the author shows that recent work tends to replace the older methods of explanation by others in which no such assumption of molecular structure is specifically involved. H. M. D.

Connexion between Colour and Degree of Dispersity. F. KIRCHHOF (*Kolloid Zeitsch.,* 1918, **22**, 98—102).—The view that the colour of disperse systems is determined by the size of the colloidal particles is considered in reference to the colours of the alkali metal sols and the changes which accompany the alteration in the valency of metal ions and the formation of complex ions. The relations exhibited suggest that the colour is fundamentally

connected with the size of the disperse particles, whether these are atomic, ionic, or colloidal in nature. II. M. D.

[Time Reactions in Colloidal Systems.] D. VORLÄNDER (*Kolloid Zeitsch.*, 1918, **22**, 103—104).—According to Reitstötter (this vol., ii, 102), a solution of potassium ferrocyanide which has been used to bring about the coagulation of colloidal aluminium hydroxide gives no blue colour on the addition of a very dilute solution of a ferric salt. In the author's opinion, the apparent absence of a reaction is to be attributed to the fact that the reaction between ferrocyanide and ferric salt is a relatively slow one, the slow rate being determined by the colloidal nature of the ferric salt solution. Salts, acids, and other substances have a considerable influence on the speed of the reaction.

The reaction between ferricyanide and ferrous salt, on the other hand, takes place instantaneously, and in this system no colloidal particles are involved. A similar difference between the speeds of corresponding reactions is found in the action of hydrogen sulphide on stannic and stannous salts. In the case of the stannous salts, the ionic reactants give rise to an immediate precipitation of the metal sulphide. H. M. D.

Rhythmic Diffusion Structures in Gelatin-Salt Jellies. II. W. MOELLER (*Kolloid Zeitsch.*, 1918, **22**, 155—163. Compare A., 1917, ii, 410).—If drops of hydrochloric acid are allowed to fall on to a semi-liquid gelatin jelly containing sodium chloride, the semi-liquid condition being produced by suitably adjusting the temperature to which the previously cooled jelly is raised, diffusion of the acid takes place with the formation of well-developed spherites which resemble closely the spheritic structures that are found in plant cells. The formation of these spherites in the diffusion of the acid through the salt-jelly is interpreted in terms of the theory of jelly structure which has been put forward in previous papers. H. M. D.

Coagulation of Roughly Dispersed Gold Hydrosols. ARNE WESTGREN and J. REITSTÖTTER (*Zeitsch. physikal. Chem.*, 1918, **92**, 750—762).—The velocity of coagulation of gold hydrosols with large diameters has been determined in the following manner. To a quantity of the sol sufficient sodium chloride solution was added to produce rapid coagulation; after measured intervals of time, 10 c.c. of the mixture were withdrawn and stabilised by the addition of gelatin, and the number of non-coagulated particles was counted. Seven series of measurements were carried out, and from the results it is shown that the theory of Smoluchowski (A., 1917, ii, 297) on the process of coagulation is fully confirmed. The radius of attraction of the particles is slightly more than twice the radius of the particles themselves, which indicates that the particles must almost touch before they unite. J. F. S.

Equilibrium of the Ternary System : Water, Sodium Sulphate, and Ammonium Sulphate. CAMILLE MATIGNON and FERNAND MEYER (*Ann. Chim.*, 1918, [ix], **9**, 251—292).—A full account of work already published (compare this vol., ii, 66, 67).

W. G.

Velocity of the Reaction between Nitric Oxide and Oxygen. M. BODENSTEIN (*Zeitsch. Elektrochem.*, 1918, **24**, 183—201 *).— With the object of settling the controversy between Lunge and Berl and Raschig on the oxidation of nitric oxide in the lead chamber, the author has determined the velocity of oxidation of nitric oxide by oxygen. The two gases were mixed at temperatures from 0° to 90° and at low pressures, and the rate of change was followed by the decrease of pressure. The reaction proceeds strictly according to the equation for reactions of the third order, $dx/dt = kC_{O_2}C^2_{NO}$, and the velocity falls considerably with increase in temperature. The velocity is not affected by the addition of nitrogen peroxide, sulphur dioxide, or water vapour. From this it is argued that the oxidation of sulphur dioxide is not catalysed by oxides of nitrogen. The experimental results of Lunge and Berl, suitably recalculated, agree very well with the present work, and those of Raschig agree fairly well beyond the point where 50% of change has occurred. The experimental methods employed by Lunge and Raschig are discussed in the light of the present knowledge of the solubilities of the higher oxides of nitrogen. From this discussion, it is shown that nitric oxide and nitrogen peroxide exist in a constant equilibrium with nitrogen trioxide, which is destroyed with great rapidity in the presence of alkali hydroxide or concentrated sulphuric acid. It is shown that only those results dealing with changes above 50%, obtained by the methods of Raschig and Lunge, are trustworthy and usable. Consequently, the view of Raschig, that nitric oxide is rapidly oxidised to the trioxide, which is then slowly oxidised to the peroxide, is no longer tenable.   J. F. S.

Velocity of Oxidation of Nitric Oxide. E. BRINER and E. FRIDÖRI (*Helvetica Chim. Acta*, 1918, **1**, 181—185).—The kinetics of the oxidation of nitric oxide have been studied. Mixtures of oxygen and nitric oxide in proportions in which they occur in the production of nitric acid from the atmosphere have been allowed to pass along a series of tubes at constant temperature, and fitted with a series of taps whereby the gases could be removed at various points. The gaseous product was divided into two portions, one condensable by an alcohol–carbon dioxide refrigerant and the other by liquid air. It is shown that if the concentration of the oxygen is regarded as constant, the reaction is of the second order, but if the oxygen concentration is considered, the reaction corresponds with one of the third order and follows the equation $dx/dt = kC_{O_2}C^2_{NO}$. With regard to the influence of temperature

* and *Zeitsch. angew. Chem.*, 1918, **31**. I, 145—148.

on the reaction, it is shown that over the interval 0° to 60°, lowering the temperature 10° increases the velocity 10—20%.

J. F. S.

The Saponification of Fats, J. P. TREUB (*J. Chim. phys.*, 1918, **16**, 107—174).—A résumé of work already published (compare A., 1917, ii, 528; this vol., ii, 71). W. G.

Influence of Foreign Substances on the Activity of Catalysts. IV. Experiments with Palladium Hydrosol in the Presence of Mercury and Mercuric Oxide. C. PAAL and WILHELM HARTMANN (*Ber.*, 1918, **51**, 711—737).—In the course of many experiments on the catalysis of mixtures of hydrogen and oxygen by colloidal palladium or platinum, it has been observed that the catalyst becomes more or less passive in time if the gases are kept over mercury, and that, in all cases, if the catalyst remains in contact with mercury, it soon becomes quite inactive, even for the hydrogenation of nitro-compounds and unsaturated substances. Consequently, the authors have made an exhaustive study of the influence of ordinary and colloidal mercury and mercuric oxide on the catalysis of hydrogen and oxygen, and a few experiments on hydrogenations by palladium hydrosol.

The results show that palladium hydrosol has a remarkable power of converting mercury and mercuric oxide into colloidal solution, the oxide much more readily, whereby the palladium permanently loses its power of activating hydrogen, and thus catalysing processes of reduction, but does not suffer as a catalyst of hydrogen peroxide. It may be that a palladium–amalgam hydrosol is formed.

The sodium protalbinate used as a protection to the palladium hydrosol has no influence of itself on mercury. It is the colloidal palladium which causes these to enter the colloidal state. This protective colloid does, however, "peptisate" mercuric oxide in an atmosphere of hydrogen. J. C. W.

Atomic Structure and Röntgen Spectra. I. A. SOMMERFELD (*Physikal. Zeitsch.*, 1918, **19**, 297—307).—A theoretical paper in which the arrangement of the rings of electrons in the atoms is discussed on a mathematical basis. H. M. D.

The First and Second Electron Rings of the Atoms. JAN KROO (*Physikal. Zeitsch.*, 1918, **19**, 307—311).—On the assumption that the high-frequency lines in the K_a series are due to the displacement of a single electron between rings which correspond respectively with one and two quanta, it is shown that experimental observations are consistent with the view that the former contains three electrons and the latter eight. H. M. D.

The Atomic Theory. X. Space-filling Numbers and the Scale of Corresponding States. RICHARD LORENZ (*Zeitsch. anorg. Chem.*, 1918, **103**, 243—248).—A formula has been deduced

from which the mean value of the space-filling number of any substance, in the solid or liquid state, can be calculated. If ϕ be the ionic volume calculated from the ionic mobility and V the volume derived from density determinations or by Kopp's formula, the space-filling number is given by ϕ/V (compare A., 1916, ii, 311, 312). For a variety of ions, the space-filling number ϕ/V_0 referred to absolute zero on the empirical scale of corresponding states has a mean value of 0.4668. It is shown that the relation between volume and temperature can be expressed by an equation of the form $V/V_s = a \cdot T/T_s + b$, where s denotes the boiling point. From this it follows that $\phi/V = \phi/V_s(a \cdot T/T_s + b)$. For solids, $a = 0.214$, $b = 0.709$, and for liquids $a = 0.453$, $b = 0.546$. Since $\phi/V_0 = 0.4668$, and V_0/V_s has a mean value $= 0.709$, $\phi/V_s = 0.331$. Hence $\phi/V = 0.331/a \cdot T/T_s + b$. An equation of state is thus derived in which the space-filling number appears as a function of temperature.   E. H. R.

Atomic Structure on the Basis of Atomic Disintegration and its Relationship to Chemical Linking, to Chemical Valency, and to the Electrochemical Character of the Elements. EMIL KOHLWEILER (*Zeitsch. physikal Chem.*, 1918, **93**, 1—42).—The author describes a theory of the structure of the atoms built up on the radioactive theory; by means of this theory, he explains the existence of atomic weights which differ from whole numbers by the assertion that such atomic weights are due to the presence of isotopes in the material examined. The abnormalities of the periodic system are explained in the same way; for example, iodine and tellurium are both mixtures of two isotopes of atomic mass 126 and 128 respectively, but in different quantities. The position of the triads of group VIII of the periodic system is explained as due to the similarity of the positive charge with dissimilarity of the masses of the middle zone and different stability of the exterior electron system. On the basis of this relationship, the author draws relationships between the structure of the atom and the valency and method of linking, to the change in valency, dissociation, and the electric charge of the atom, and to the relationship between the electrochemical character and the valency of the elements. The tendency of certain elements to act with one valency in preference to another is also considered. For details of these points, the original must be consulted.   J. F. S.

The Definition of the Term " Chemical Element." RUD. WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1918, **92**, 741—749).— A theoretical discussion based on the definition of an element put forward by Paneth (A., 1916, ii, 240). It is asserted that this definition in no way corresponds with that of most chemists, who retain the old definition as sufficient to express the chemical idea of an element.   J. F. S.

Definition of the Term " Chemical Element." FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, **93**, 86—88).—An answer

to Wegscheider's criticism (see preceding abstract) of the author's paper on this subject (A., 1916, ii, 240).   J. F. S.

Tables of Elements and Atoms. FRITZ PANETH (*Zeitsch. physikal. Chem.*, 1918, **92**, 677—684).—The author proposes to substitute the present atomic weight table by two tables, (1) a table of combining weights containing those elements of which no isotopes exist, and using as combining weights the experimentally determined atomic weight, and (2) an atom table containing the whole of the elements, including all the isotopes with their theoretical atomic weights. The reasons for the proposed change are threefold : (1) There are more kinds of atoms than elements, (2) the combining weight of some elements is not the same as the atomic weight, and (3) in many cases there is no experimental confirmation of perfectly sound atomic weights which have been deduced from theoretical considerations.   J. F. S.

Twenty-fifth Annual Report of the Committee on Atomic Weights. Determinations Published during 1917 GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1918, **40**, 1009—1014).— These comprise hydrogen, helium, carbon and sulphur, bromine, zirconium, tellurium, and samarium. Only in the case of zirconium has evidence been presented during the past year which seems to demand an important alteration in the previously accepted atomic weight. By conversion of the tetrachloride into the dioxide, Venable and Bell have obtained the value 91·76 for the atomic weight of zirconium (A., 1917, ii, 479), which is more than a unit higher than the value given by the International Committee on Atomic Weights.   C. S.

The Periodic System and Genesis of the Elements. CURT SCHMIDT (*Zeitsch. anorg. Chem.*, 1918, **103**, 79—118).—The author's hypothesis of the genesis of the elements (A., 1911, ii, 198) has been considerably amplified. The elements do not belong to a single system, but to four partial systems genetically connected. The primary or hydrogen system is only represented by hydrogen, which is regarded as the sole survivor of a past evolutionary period of matter. In it, the metallic and metalloid properties of matter have not become differentiated. Baur, from a study of logarithmic atomic volume curves, drew the conclusion that two different generations of elements can be distinguished (A., 1911, ii, 480). These two generations practically correspond with the author's secondary or helium partial system, comprising the elements He–Ti, As–Zr, Sb–Ce, Bi–Th, and the tertiary or iron system, comprising the remainder of the elements, with the exception of the rare earth metals, which form a distinct quaternary system. When this hypothesis is adopted, the problem of the double periodicity of the elements disappears; for instance, the metals copper, silver, and gold no longer appear in the same group as the alkali metals, since the former belong to the tertiary, the latter to the secondary partial system. The inert gases appear as the central group of the He

system with valency $= 0$, contravalency $= \pm 8$, whilst the iron, palladium, and platinum triplets occupy a corresponding position in the tertiary system, with maximum valency $= \pm 8$, contravalency $= 0$. The three blank spaces with which the He system begins are identified with elements detected spectroscopically in the nebulæ and the hottest fixed stars. These, with their probable atomic weights, are nebulium, the parent of nitrogen, Nu, $1\cdot31$ or $1\cdot63$; ekaoxygen, Eo, $2\cdot36$; and ekafluorine, Ef, $2\cdot95$.

Two principles are postulated, according to which the elements have probably been evolved: (1) the ontogenetic principle, involving the formation of the primary members of the different groups by direct condensation of protyl; (2) the phytogenetic principle, by which the higher members of the groups are developed from the lower by a process of integration. Evolution has taken place, not horizontally through the series, but vertically through the groups, each member of a horizontal series being independent of its neighbours. It follows that the atomic weights of potassium and argon, and of tellurium and iodine, present no anomaly. Some hitherto puzzling stellar phenomena also find their explanation in these principles; for instance, the occurrence of calcium and magnesium in certain stars which do not reveal the presence of oxygen and other elements of low atomic weight. The hypothesis is also in agreement with the relative abundance and distribution of the elements on the earth, and explains the frequent occurrence together of consecutive elements of the same group, such as zinc and cadmium. The direction of evolution was certainly from simpler to higher forms, following the course of cosmic evolution, and it is probable that, in atomic as in biological evolution, a process of selection with the survival of the fittest has been operative. There have probably been formed from time to time elements which, not being adaptable to the prevailing cosmic conditions, have undergone transformation. The radioactive elements are probably examples of such unsuitable types, and are at present passing through an evolutionary stage.

A rational system of nomenclature for the radioactive elements and their degradation products is suggested. Radium emanation is given the name *Radon*, Ro, which at once indicates its origin and its relationship to the argon group. The other emanations become *Thoron*, To, and *Acton*, Ao, respectively. The other degradation products are given names indicative of their derivation, manner of formation, and of the group of isotopes to which they are related. Thus radium-D becomes β-*radiotrilead*, with the symbol β-Ro$'''$Pb, and radium-C_2 becomes β-*radiotrithallium*, β'-Ro$'''$Tl, the accented β indicating that the product does not belong to the principal radium series, but to a side-chain. A complete list of new names for all the known products from uranium, actinium, and thorium is given.   E. H. R.

New Table of the Periodic System. Ingo W. D. Hackh (*J. Amer. Chem. Soc.*, 1918, **40**, 1023—1026).—Arranged in

vertical rows on either side of the central column of the non-valent elements are, on the right-hand side, the elements of the groups IA, 2A, 3A, and 4 in the upper half of the table, and those of groups 1B, 2B, 3B, and 4 in the lower half, and, on the left-hand side, the elements of the groups 7A, 6A, 5A, and 4 in the upper half, and those of 7B, 6B, 5B, and 4 in the lower half. The elements of group 8 appear in the middle of the lower half of the table. This arrangement of the elements shows (1) a sharp classification of the elements into non-metals, noble gases, light metals, and heavy metals; (2) only five gaps, indicating that only five elements remain to be discovered; (3) elements having high electro-potential, simple spectra, and colourless ions appear in the upper half of the table, whilst those having low electro-potential, complex spectra, coloured ions, and tendency to form complex salts appear in the lower half; (4) on the left side of the table are the electronegative elements, those of the upper half forming strong acids, those of the lower half weak oxy-acids; on the right side of the table are the electropositive elements; (5) the middle of the lower half of the table is occupied by the amphoteric elements.

A peculiarity of the table is that the similarity of the elements is in the vertical direction in the upper half of the table and in the horizontal direction in the lower half.   C. S.

Progress of Chemistry during the Past One Hundred Years. HORACE L. WELLS and HARRY W. FOOTE (*Amer. J. Sci.*, 1918, [iv], **46**, 259—302).—A brief account is given of the general lines of development of chemical knowledge during the last hundred years.   H. M. D.

New Filters. R. ZSIGMONDY and W. BACHMANN (*Zeitsch. anorg. Chem.*, 1918, **103**, 119—128).—A new type of filter is described, termed a membrane filter, prepared by drying, under conditions not specified, solutions of certain colloids. The membranes thus obtained have a parchment-like appearance and a smooth surface, and are strong and durable. They can be prepared of any desired thickness and with any desired size of pore. The filters are very rapid in action and are particularly suitable for vacuum filtration, as they will stand high pressures. The membrane chosen for any particular filtration should be such that the pores are smaller than the diameter of the particles to be filtered. Under these conditions, no adsorption takes place, the pores do not get choked, and the membrane can be washed and used again with undiminished filtration velocity. A filter which, under 70 cm. pressure and with an area of 80 sq. cm. will pass 100 c.c. of water in eight seconds (an 8 sec. filter), will filter completely a graphite sol in which the particles are 200—300 $\mu\mu$ in diameter. A similar membrane will also stop gold particles of 80—100 $\mu\mu$, but allows particles 30—40 $\mu\mu$ to pass through.

The membranes can also be used for separating the constituents of a mixed colloidal solution. Thus when a solution containing

Prussian blue and benzopurpurine was filtered through a 5 sec. filter (a relatively coarse membrane), the former was stopped completely, whilst the latter passed through. This was collected completely on a 3 min. filter. It is anticipated that the new filters will be valuable for many laboratory and technical purposes.

E. H. R.

Inorganic Chemistry.

The Influence of Different Modifications of Sulphur on the Melting Point of Sulphur. ERNST BECKMANN, RUDOLF PAUL, and OTTO LIESCHE (*Zeitsch. anorg. Chem.*, 1918, **103**, 189—206). —The "natural freezing point" of sulphur, 114·5°, is 4·75° below that of normal sulphur, S_λ. Assuming that the depression of the freezing point is due to the presence of $S_\pi = 128$, the cryoscopic constant of sulphur being 213 (this vol., ii, 218), the proportion of S_π present must be 2·78%. This is in good agreement with Aten's conclusions, but not with that of Smith and his co-workers, who decided that "natural" sulphur contains about 3·6% of amorphous sulphur, S_μ. The conclusion that "natural" sulphur does not contain S_μ is also supported by the results of experiments on the effect of the addition of various forms of sulphur to sulphur of f. p. 114·5°, the additions being made to samples, prepared under standard conditions, at a temperature just above the melting point. Amorphous sulphur, prepared in a variety of ways, has practically no effect on the freezing point, and is shown to be rapidly transformed into a mixture of S_λ and S_π of the same composition as the fused mass. If the fusion is rapidly cooled after the addition of the S_μ, only about 24% of the added sulphur is still insoluble in carbon disulphide. When added to a fused mass having a lower f. p. than 114·5°, S_μ has no effect, but when added to one having a higher f. p., it has the effect of lowering it towards the "natural" f. p., indicating that at the higher temperature relatively more S_π is formed from the S_μ.

When S_μ is heated, it shows no sharp melting point, but, having reached 120°, it has at once the "natural" freezing point 114·5°. If a mixture of rhombic sulphur with about 5% S_μ is melted, it has a freezing point about 2° lower than that of a sample of rhombic sulphur similarly treated, indicating that under these conditions the S_μ decomposes into 23% S_π and 77% S_λ.

A sample of S_π prepared according to Aten's method (A., 1915, ii, 254) when added to a sample of "natural" sulphur lowered the f. p. slightly, indicating, however, only about 4·6% S_π in the preparation. Both rhombic and monoclinic sulphur raise the f. p. of "natural" sulphur by increasing the proportion of S_λ.

A sample of Engel's sulphur, S_ρ, having a molecular weight of

192, was found to lower the f. p. of natural sulphur, but owing to the rapidity with which it decomposes, only 73% of the calculated depression could be observed. The decomposition of this form of sulphur is not a simple unimolecular reaction, and S_μ appears to be an intermediate product. E. H. R.

Flame Reactions. JACOB PAPISH (*J. Physical Chem.*, 1918, **22,** 430—432).—When the vapour of selenium dioxide is introduced into a Bunsen flame, an intense blue colour is produced. Elementary selenium is deposited on a cold surface which is brought into the blue flame. In similar circumstances, the vapour of tellurium dioxide produces a blue-coloured flame tinged with green in its uppermost part, and a bright, metallic mirror is deposited on a cold surface held in the hottest part of the flame. The reduction of the oxides in the flame is supposed to be the cause of the characteristic luminescence. H. M. D.

Occurrence of Hydrogen Selenide in Rain and Snow. TH. GASSMANN (*Helvetica Chim. Acta*, 1918, **1,** 52—54).—One hundred c.c. of rain are concentrated to 80 c.c., and a strong current of sulphur dioxide is passed through the liquid for fifteen minutes. On keeping over night, a reddish-brown precipitate forms, which is shown to be selenium in the following way. It is oxidised with aqua regia and the solution precipitated with hydrogen sulphide; the precipitate is dissolved in fuming nitric acid, and the selenium precipitated either by hydrochloric acid or stannous chloride. Snow may be similarly treated.

Selenium may also be detected by precipitating the concentrated rain or snow water with a concentrated solution of barium chloride. The precipitate is collected after keeping over night, washed with ether, and dried in a desiccator over soda-lime. On treatment with concentrated hydrochloric acid, hydrogen selenide is evolved, which blackens a lead acetate paper.

It is probable that hydrogen selenide is not present as such in the rain or snow, but is in combination with a second component which has not yet been identified. T. S. P.

A New Oxide of Selenium. FRITZ VON KONEK (*Ber.*, 1918, **51,** 872—876).—When diantipyryl selenoselenide, $R_2Se:Se$ (this vol., i, 407), was burnt in a bomb in oxygen under 25—30 atm. pressure, with the idea of converting the selenium into selenic acid, a white, amorphous deposit was found adhering firmly to the walls of the crucible. This proved to be an *oxide*, approximating to the formula Se_3O_4, which is almost insoluble in water, and is decomposed by boiling sodium hydroxide, about one-third of the selenium being deposited in the free state, the remainder giving rise to sodium salts of selenium acids. Strange to say, diantipyryl monoselenide, and diselenides of the type $R\cdot Se\cdot Se\cdot R$, provided by Lesser (A., 1912, i, 642) and Bauer (A., 1913, i, 263), gave no trace of this oxide. J. C. W.

Nitrogen Chloride, with a Convenient Method for its Preparation. HASHMAT RAI (*Chem. News,* 1918, **117**, 253).— About 10 c.c. of a freshly prepared, filtered, concentrated solution of bleaching powder in a large test-tube are cooled in ice to about 0°, and an equal volume of cold, saturated ammonium chloride solution is added. When the vigorous reaction has subsided, after ten minutes, the nitrogen chloride is exploded by the addition of turpentine. The chloride on the surface explodes instantly, that at the bottom more violently after some time, the interval between the two explosions depending on the height of the liquid column, the amount of turpentine added, the nature of the surface explosion, and the amount of nitrogen chloride present. All apparatus must be absolutely free from grease and direct sunlight should be entirely excluded.   C. S.

Catalytic and Thermal Syntheses of Ammonia. E. B. MAXTED (*J. Soc. Chem. Ind.,* 1918, **37**, 232—235T).—The author discusses the effect of the time of contact, temperature, and pressure on the percentage of ammonia formed and on the yield per litre of catalyst space in connexion with the catalytic synthesis of ammonia. Experiments are described on the thermal synthesis of ammonia at arc temperatures.   J. F. S.

Determination of the Surface Tension and Critical Density of Ammonia. ALFRED BERTHOUD (*Helvetica Chim. Acta,* 1918, **1**, 84—87).—The critical density of anhydrous ammonia has been determined by Young's method, as modified by Ter-Gazarian, the densities of the liquid and vapour being measured between 0° and the critical temperature, 132·3°. The critical density (d_c) is found to be 0·2362, whereas the calculated value, (d_{th}), assuming that the gas laws hold up to the critical point, is 0·05609. The ratio of d_c to d_{th} is 4·211, whereas the value of this ratio for normal liquids is approximately 3·6. This indicates that ammonia is associated even at the critical point, and the association is confirmed by measurements of the surface tension; K, in the Eötvös-Ramsay formula, is found to be 1·80 between 11° and 59°, giving a value of 1·27 for the association factor. Trouton's rule also gives a value of 23·8, which is higher than the normal value for unassociated liquids.   T. S. P.

Reduction of the Oxides of Nitrogen to Ammonia. Stability of Nitric Oxide. PH. A. GUYE and FRITZ SCHNEIDER (*Helvetica Chim. Acta,* 1918, **1**, 33—52).—In Switzerland, the conditions are such that oxides of nitrogen can be manufactured more conveniently than ammonia, so that a knowledge of the conditions under which the former are reduced to the latter becomes necessary. The authors have carried out such an investigation, using a special apparatus in which known mixtures of hydrogen with the respective oxides of nitrogen were passed over heated

reduced nickel as catalyst. The ammonia formed was estimated by absorption in a known volume of standard sulphuric acid. In some cases, this estimation was controlled by heating the solution with excess of sodium hydroxide and again absorbing the ammonia in standard acid; this was necessary in the case of nitrogen peroxide, since some ammonium nitrate is forming during the reduction.

In order to be quite certain of the results obtained, it was necessary to carry out preliminary experiments on the action of heat alone on some of the oxides of nitrogen used, since the statements found in the literature on this subject are somewhat contradictory and often have reference to the results obtained when the gas is heated under pressure. An apparatus was used in which the gas could be heated under atmospheric pressure, since the experiments on reduction were carried out at this pressure. It consisted of a cylindrical glass bulb heated in an electric furnace. Sealed on to the bottom of the bulb was a narrow glass tube, which could be cooled in liquid air or other cooling medium; products such as nitrogen peroxide could then be frozen out and identified.

In order to decompose nitric oxide under atmospheric pressure, it is necessary to raise the temperature to 575° and keep it there for several hours, even in the presence of spongy platinum as catalyst. Under these conditions, and contrary to what takes place under pressure, there is no formation of nitrous oxide. The primary products of decomposition are nitrogen and oxygen; on cooling, the oxygen reacts with undecomposed nitric oxide to give nitrogen peroxide. Nitrous oxide decomposes simply into nitrogen and oxygen.

In the reduction of the oxides NO, N_2O, and NO_2 by hydrogen, with nickel as catalyst, two reactions take place simultaneously, the one giving ammonia and the other nitrogen; for example, $2NO + 5H_2 = 2NH_3 + 2H_2O$, $2NO + H_2 = N_2 + H_2O$. Both in the reduction of nitric oxide and of nitrogen peroxide, the formation of intermediate products, namely, nitrous oxide and nitric oxide respectively, does not occur.

In all these reactions, the condition of the reduced nickel plays an important part, and two different preparations do not necessarily give the same results. Also there is an optimum yield of ammonia which depends on the composition of the gaseous mixture and on the velocity with which the gases are circulated over the nickel.

Temperatures of 250—300° appear to be the best for the formation of ammonia. Below these temperatures, the reduction takes place slowly, whilst above these temperatures, the nickel gradually loses its activity and the ammonia is appreciably decomposed into its elements.

Nitric oxide gives the best yields, 70% of the gas, on an average, being transformed into ammonia; 25—39% of nitrogen peroxide and only 3—7% of nitrous oxide is reduced to ammonia.

The reduction of the oxides of nitrogen to ammonia does not therefore appear to be an advantageous process from the manu-

facturing point of view, except perhaps in the case of nitric oxide, where a more systematic study of the conditions may give better results.   T. S. P.

The Revision of the Atomic Weight of Carbon from the Densities of Acetylene, Ethylene, and Ethane. KNUT STAHRFOSS (*J. Chim. phys.*, 1918, **16**, 175—200).—The values obtained for the weight of a normal litre of gas are: for acetylene, 1·1791 grams; for ethylene, 1·2610 grams; for ethane, 1·3565 grams. From these, the atomic weight of carbon is calculated as 12·00, but this value will be subject to revision when it has been possible to determine directly the departure from Avogadro's law in the case of these gases, and when new determinations of the density of ethylene have been made.   W. G.

Ultra-microscopic Investigation of very thin Metal Films obtained by Evaporation in High Vacuum. II. W. REINDERS and L. HAMBURGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1135—1154. Compare A., 1917, ii, 405).—The thin films of metal which are deposited on a glass surface when various metals are strongly heated in a highly exhausted space have been examined according to the method previously described (*loc. cit.*). It is found that elements which melt at high temperatures, such as tungsten, molybdenum, platinum, nickel, iron, and carbon, give rise to films which under the ultra-microscope are either entirely or for the most part devoid of structure. Elements of lower melting point show, on the other hand, a tendency to form films which have a clearly recognisable structure with ultra-microns as the structural units. The elements belonging to this group which have been examined are silver, gold, copper, magnesium, zinc, and cadmium. When the temperature of the glass surface on which the metal vapours condense was cooled by means of liquid air, the silver, copper, and gold films obtained were similar to those of the elements of high melting point in the first group. The lowering of the temperature of the condensing surface did not, however, eliminate the structural characteristics from the films of magnesium, zinc, and cadmium, although the coarseness of the structure was considerably reduced. The films devoid of structure show distinct signs of heterogeneity when the temperature is raised, this effect being very clearly marked in the case of films of silver, gold, platinum, iron, and molybdenum.

The films produced by tungsten, molybdenum, platinum, nickel, and iron are colourless, whilst those obtained from the other metals examined are coloured. That this colour does not depend on the structure or absence of structure is shown by the fact that the films of copper, silver, and gold have the same colour, whether these films are structureless or are ultra-microscopically heterogeneous. The colour effect is consequently due to the selective absorption of the atoms and is a characteristic property of the metal.   H. M. D.

A Complete Review of Solutions of Oceanic Salts. IV. ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1918, **103**, 1—54. Compare this vol., ii, 70).—The influence of temperature on the equilibrium of the system $(Na_2-K_2-Mg)(Cl_2-SO_4)$ is given a graphic representation by the method developed in previous papers. The numerous diagrams given are fully explained in the paper.

E. H. R.

The Nature of Subsidiary Valencies. XIX. Ammines of Silver. FRITZ EPHRAIM (*Ber.*, 1918, **51**, 706—710).—The vapour tensions of the triammines of some silver salts have been measured by the author's usual method. A few of the compounds had only recently been prepared by Bruni and Levi (A., 1916, ii, 482), whilst others had long been known. The following list gives the temperatures at which the vapour tensions of the triammines are 760 mm.: perchlorate, 79·5°; chlorate, 65·5° (by extrapolation; highest reading, 51·5°); chloride, 17·7°; bromide, 3·7°; bromate, 1°; permanganate, 12°; nitrate, 63°; nitrite, 69·3°. The iodide, iodate, and periodate form no triammines.

When the acid radicle is truly anionic, it is usually found that the stability of the ammines rises from chlorides to iodides and from chlorates to iodates. The complete reversal of this order in the case of the silver salts suggests, therefore, that there is a complex cation present, at any rate in the solid compounds, as expressed, for example, in the formula

$$(NH_3)_3 \left[Ag \overset{\cdots Cl \cdots}{\underset{\cdots Cl \cdots}{\diagdown\diagup}} Ag \right] (NH_3)_3$$
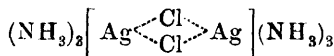
J. C. W.

The Crystal Form of Barium Iodide Hexahydrate. O. MÜGGE (*Centr. Min.*, 1918, 105—107).—Commercial barium iodide crystallises at the ordinary temperature in large, hexagonal prisms without distinct end faces. The crystals are apparently isomorphous with $SrCl_2,6H_2O$. The prism faces show diagonal striation always in the same direction on all faces of all crystals. The crystal class is probably trapezohedral tetartohedral; $a : c = 1 : 0·538$ (approx.); double refraction fairly strong, negative. The crystals melt in their water of crystallisation at 25·7°. E. H. R.

Double Carbonates of Sodium and Potassium with the Heavy Metals. MALCOLM PERCIVAL APPLEBEY and KENNETH WESTMACOTT LANE (T., 1918, **113**, 609—622).—An examination of the preparation and properties of the double salts $Na_2Cu(CO_3)_2,3H_2O$, $Na_2Co(CO_3)_2,4H_2O$, and $K_2Co(CO_3)_2,4H_2O$ (compare Deville, *Ann. Chim. Phys.*, 1851, [iii], **33**, 75; Reynolds, T., 1898, **73**, 262; Gröger, A., 1907, ii, 240; Wood and Jones, A., 1907, ii, 620; Luther and Kršnjavi, A., 1905, ii, 705). The solubility equilibria are investigated for the sodium–copper and potassium–cobalt salts in the additional presence of the corresponding alkali hydrogen
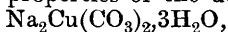
carbonate, this being necessary in order to reduce the tendency to the separation of basic compounds.

For experimental details, reference should be made to the original.   D. F. T.

Utilisation of Waste Nessler Solution. WILLIAM CLIFFORD (*J. Soc. Chem. Ind.*, 1918, **37**, 179T).—Nessler solution residues are treated with a few c.c. of sulphuric acid, whereby the mercuric iodide is precipitated. The mercuric iodide may be converted into sodium iodide as follows: 200 grams of the iodide are placed with 500 c.c. of water in a litre flask, and 20 grams of iron filings added. The mixture is heated for sixty minutes on a water-bath, when the reaction is complete, mercury being precipitated and ferrous iodide formed in solution. The green solution obtained by filtration is boiled and kept overnight, when it becomes ruby-red. The iron is then precipitated by sodium carbonate or hydroxide. Generally a second precipitation is necessary to remove all the iron. The filtrates from the second precipitation may be used directly for oxygen absorption determinations. Nessler solution may be prepared with sodium iodide and hydroxide just as well as with the potassium compounds.   J. F. S.

Ceric Oxychloride, produced in the Electrolysis of Cerous Chloride. HANS ARNOLD (*Zeitsch. Elektrochem.*, 1918, **24**, 137—138).—When molten cerous chloride is electrolysed, a secondary reaction occurs at about 900° as long as there is an excess of water present in the molten mass. The product of this secondary reaction is a dark brown, amorphous powder which is deposited on the cooler parts of the anode. The product is very hygroscopic, and on analysis is shown to be a mixture of ammonium chloride, ceric oxychloride, and water. All attempts to remove the ammonium chloride by washing or sublimation converted the basic ceric chloride into cerous chloride. It is suggested that the product is produced from ceric chloride, formed on the anode, by the action of water, thus: $CeCl_4 + H_2O = CeOCl_2 + 2HCl$. The product always contains water, and analysis indicates that the water is combined and is present as $CeOCl_2,10H_2O$. The compound is highly deliquescent and is hydrolysed by water with the formation of ceric hydroxide and cerous chloride.   J. F. S.

Carbides. OTTO RUFF (*Zeitsch. Elektrochem.*, 1918, **24**, 157—162).—A preliminary paper on the temperature of formation and the stability range of carbides. The present paper deals with the equilibria between carbon and aluminium and between chromium and carbon. Aluminium carbide, Al_4C_3, sublimes at temperatures up to 2200° without melting and with some decomposition. This decomposition is independent of temperature. The melting point of aluminium carbide lies above this temperature. A vapour pressure curve has been constructed up to 2300°. At 2200°, aluminium carbide is in equilibrium with graphite,

aluminium saturated with graphite and vapour under a pressure of 400 mm. In the case of chromium and carbon, a composition-temperature diagram has been constructed for the pressure 10 mm. At 2270°, the mixture boils, and the vapour consists entirely of chromium. Between 2050° and 2250°, the fusion remains constant in composition and corresponds with Cr_3C_2. Below 2050° down to 1875°, graphite and the carbide, Cr_3C_2, exist side by side as solid phases. The compound Cr_5C_2 is also shown to exist.　　J. F. S.

The Determination of the Crystal Structure of Complex Compounds. PAUL NIGGLI (*Physikal Zeitsch.*, 1918, **19**, 225—234). —The point system characteristic of any crystal can be determined from a knowledge of the crystal class and of the ratios of the distances between successive reflecting planes of atoms in the crystal in different directions as determined by the X-ray reflection method. As an example, the case of potassium alum, already examined by Vegard and Schjelderup (this vol., ii, 156), is worked out. The point system is the one designated T_h^6, and the elementary cube contains four molecules of the form $[Al(H_4O_2)_6](SO_4)_2K$. The aluminium, potassium, and sulphur atoms can be immediately identified with appropriate points in the point system. The oxygen atoms of the SO_4 group appear to be of two kinds, three being alike, distributed symmetrically about a trigonal axis, the fourth being situated on the trigonal axis, and the four together forming a trigonal pyramid with the sulphur atom at the centre. The oxygen atoms of the water molecules probably correspond with two distinct groups of unfixed points in the system. The exact positions of the sulphur and oxygen points are not fixed by the symmetry of the system, but equations are developed by means of which their co-ordinates may be calculated when the relative intensities of the X-ray reflection spectra of different orders are known for the faces (100), (110), and (111). The author's solution of the alum structure differs to some extent from that put forward by Vegard and Schjelderup in the disposition of the oxygen atoms.
　　　　　　　　　　　　　　　　　　　　E. H. R.

Crystal Structure of the Alums and the Rôle of the Water of Crystallisation. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1918, [iv], **55**, 397—400).—Polemical. The authors point out that the results of Vegard and Schjelderup (this vol., ii, 156) on the rôle of the water of crystallisation in the building up of the space grating of alums are not new, but were published by them in an earlier paper (A., 1916, ii, 505). A criticism of the spacial model of alums put forward by the same authors concludes the paper.　　　　　　　　　J. F. S.

Basic Exchange in Permutite. I. V. ROTHMUND and G. KORNFELD (*Zeitsch. anorg. Chem.*, 1918, **103**, 129—163).—The basic exchange which takes place between a hydrated alumino-

silicate such as permutite (compare Gans, A., 1914, ii, 55) and a
neutral salt solution is to be regarded as a true chemical change
and not as an adsorption phenomenon as suggested by Wiegner
(A., 1912, ii, 981).   In the case of permutite, an equilibrium
rapidly becomes established with the solution. The resulting mixed
permutite functions as a single solid phase, and is to be regarded
as a solid solution, the composition of which depends on the relative
concentrations of the cations in the solution.   In the case of uni-
valent cations, the composition of the permutite is independent of
the total concentration of the solution, but when bivalent cations,
for example, calcium, are present, the total as well as the relative
concentration must be taken into account.   The experimental work
was confined to univalent metals, the equilibrium between silver
permutite and the nitrates of potassium, rubidium, lithium,
ammonium, and thallium, and between sodium permutite and
ammonium and thallium nitrates, being investigated. If c_1 and
c_2 represent the concentration of two bases in solution, and c'_1
and c'_2 their concentrations in the permutite in equilibrium with
the solution, the empirical relation found is $c'_1/c'_2 . (c_2/c_1)^\beta = K$,
in which β is less than unity.   The values of β and K vary con-
siderably in tne different cases examined.   A bibliography of the
subject of basic exchange is appended to the paper.   E. H. R.

Place of Manganese in the Periodic System. F. RUSSELL
VON BICHOWSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 1040—1046).—
The arguments usually given for placing manganese in the seventh
group are based on the periodic law, isomorphism, and chemical
properties, and appear open to question in the light of modern
knowledge.   On the other hand, twelve different lines of argument
based on purely chemical relationships are given by the author for
placing manganese in the eighth group with iron, nickel, and
cobalt.   Moreover, the atom colours of the various valences of
manganese show that the normal valence must be even, not odd
(Bichowsky, this vol., ii, 142).

An improved form of the periodic table is presented showing the
relations of the eighth and the rare earth groups to the rest of
the periodic system.   C. S.

**Structure of Tungsten Steels and the Change under
Heat Treatment.** KÔTARÔ HONDA and TAKEJIRÔ MURAKAMI (*Sci.
Rep. Tohôku Imp. Univ.*, 1918, **6**, 235—283).—Tungsten steels
containing 0·12 to 1·57% of carbon and 0·23 to 30·0% of tungsten
have been systematically investigated in respect of their magnetic
susceptibility and micro-structure, and attention has been paid to
the change o structure at high temperatures.

According to microscopic observations, the system iron–tungsten
is characterised by the formation of a single compound, Fe_2W.   The
tungsten in tungsten steels may be present either in the form of
iron tungstide or tungsten carbide, WC, or in both forms.   The
tungstide is soluble in iron to an extent represented by 9% of

tungsten, and in steels which contain a larger proportion of tungsten than corresponds with this limiting value the tungstide is present as a separate phase in globular form. As the carbon content increases, a larger proportion of tungsten is required for the appearance of the globules, this fact being due to the formation of tungsten carbide.

In the normal condition, the tungsten carbide is present in the form of the double carbide, $4Fe_3C,WC$, which decomposes at 400°. At high temperatures, tungsten carbide reacts with iron in accordance with the equation $WC + 5Fe = Fe_3C + Fe_2W$, and when the steel is subsequently cooled, the transformation points are lowered by the dissolving of the iron tungstide in the iron.

The changes which occur under the influence of various methods of heat treatment are described in reference to a large number of magnetic susceptibility curves and photomicrographs. The authors consider that the occurrence of the double carbide, $4Fe_3C,WC$, has been clearly proved by their investigations. H. M. D.

Adsorption Compounds. Ferriarsenites. TADEUSZ ORYNG (*Kolloid Zeitsch.*, 1918, **22**, 149—154).—When a solution of a ferric salt is mixed with a solution of sodium arsenite and sodium hydroxide added to the mixture, a precipitate is obtained which contains ferric and arsenious oxides, and this has been regarded as an adsorption compound, the arsenious oxide being adsorbed by the precipitated ferric hydroxide. The systematic investigation of the composition of the precipitate in relation to that of the mother liquor has led the author to the conclusion that the facts cannot be satisfactorily explained in terms of the adsorption theory, and that the precipitate consists of a mixture of definite chemical compounds represented by the general formula $xFe(OH)_3,yAs_2O_3'''$. In the author's opinion, many supposed cases of adsorption are probably examples of chemical changes of a similar type.

H. M. D.

Peptisation of Ferric Arsenate and Phosphate and Formation of their Gels. HARRY N. HOLMES and ROSSLEENE ARNOLD (*J. Amer. Chem. Soc.*, 1918, **40**, 1014—1019).—A continuation of previous work (Holmes and Rindfusz, A., 1916, ii, 624). It is now found that unwashed precipitates of ferric arsenate or phosphate are stabilised by any soluble arsenates or phosphates that may be present, and therefore much more concentrated alkali hydroxide may be used as peptising agent, and it may be added more rapidly and in greater excess. The presence of thoroughly adsorbed alkali arsenate in precipitated ferric arsenate compels the use of more sodium hydroxide for peptisation, but the resulting colloid is stable in direct proportion to the amount of alkali arsenate present. Furthermore, if it is ammonium arsenate that is present in excess, less base is required for peptisation than in the case of other alkali arsenates, the order being NH_4, K, Na, Li. Ferric arsenate or phosphate can be peptised by sodium hydroxide or ferric chloride.

With sodium hydroxide, the action is greatly aided by sucrose or glycerol, but is hindered by sodium chloride. On dialysis of the colloids formed by the action of sodium hydroxide on ferric arsenate or phosphate, no gels form except in the presence of sucrose or glycerol.

Dialysis of the colloids formed by the ferric chloride peptisation of ferric arsenate or phosphate yields excellent gels. With barely enough ferric chloride for complete peptisation, the gels are opalescent and yellowish-grey, forming in a few days. With an excess of ferric chloride, the gels are red, weaker in structure, and slower in formation in direct proportion to this excess. Gels form in much less time when the original precipitate of ferric arsenate contains thoroughly adsorbed alkali arsenate; this accelerating influence of alkali arsenates decreases in the order $NH_4 > K > Na > Li$.

C. S.

Nitrosopentamminecobalt Salts. A. WERNER and P. KARRER (*Helvetica Chim. Acta*, 1918, **1**, 54—78).—Sand and Genssler (A., 1903, ii, 549; 1904, ii, 39) have described two series of salts which they obtained by the action of nitric oxide on ammoniacal solutions of cobalt salts; the one series was red and the other black in colour, and both corresponded with the formula $[NO \cdot Co(NH_3)_5]X_2$. It was considered that the two series were valency isomerides, and the present authors have taken up the question again in order further to investigate the question of valency. They find that Sand and Genssler's statements with respect to the black series are correct, and some new salts are described, of which the iodate is very stable; most of the statements with respect to the red series are found to be incorrect.

Black Nitrosopentamminecobalt Salts.—The chloride,
$$[NO \cdot Co(NH_3)_5]Cl_2,$$
is obtained by the method described by Sand and Genssler. In stoppered bottles it is quite stable, but on exposure to the air transformation to the red salt takes place, accompanied by partial decomposition. The transformation is due to moisture, and is not dependent on the action of light. The nitrate and sulphate are very unstable and cannot be obtained pure. The *iodate*,
$$[NO \cdot Co(NH_3)_5](IO_3)_2,$$
is precipitated almost immediately when nitric oxide is passed through a strongly ammoniacal solution of cobalt iodate, air being carefully excluded during the operation. It forms a blackish-brown, crystalline powder, and is quite stable in the absence of moisture. Attempts to prepare the bromide, iodide, cyanide, and chlorate were unsuccessful.
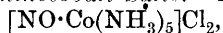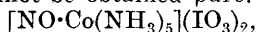
Dinitrosodecamminedicobalt Salts (*Red Salts*). YX_4, where $Y = [N_2O_2 \cdot Co_2(NH_3)_{10}]$.—The nitrate, $Y(NO_3)_4$, is obtained by Sand and Genssler's method, but the yields are very variable. It is best purified by precipitation from aqueous solution with sodium nitrate. When 20—25% nitric acid is added to the aqueous solution, an orange-coloured precipitate of the *acid nitrate*, $Y(NO_3)_4, HNO_3, H_2O$, is formed, which readily loses its water of crystallisation over

calcium chloride; over phosphoric oxide, some nitric acid also seems to be lost. The compound described by Sand and Genssler, namely, $[Y(NO_3)_4,2HNO_3] - H_2O$, does not exist, nor could the pure additive products of the nitrate with silver nitrate and lead nitrate, described by these authors, be obtained.

The *acid perchlorate*, $Y(ClO_4)_4,HClO_4,H_2O$, falls as a reddish-brown powder when the cold, concentrated solution of the nitrate is precipitated with 30% perchloric acid solution. The compound $[Y(ClO_4)_4,2HNO_3] - H_2O$ does not exist. The compound

$$(NO_3)_2[Co(NO)(NH_3)_5]$$

$$(NO_3)_2\left[CoN{<_I^I}(NH_3)_5\right],$$
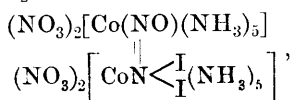
described by Sand and Genssler as being prepared by the action of potassium iodide and nitric acid on the nitrate could not be obtained. Probably a periodide is produced, which, however, is very unstable and cannot be obtained pure By precipitation of a solution of the nitrate with potassium iodide, the *iodide*, $YI_4,4H_2O$, is obtained as a brownish-yellow, flocculent precipitate; it is only obtained pure after several reprecipitations with potassium iodide. The compound, $Y(NO_3)_2I_2,KI$, does not exist.

The double sulphate, $Y(SO_4)_2,[N_2O_2Co_2(NH_3)_9(OH_2)](SO_4)_2,2H_2O$, prepared by Sand and Genssler by the action of nitric oxide on an ammoniacal solution of cobalt sulphate, could not be obtained. The *sulphate*, $Y(SO_4)_2,2H_2O$, was obtained from the nitrate by the aid of nitron sulphate; after collecting the nitron nitrate, the filtrate is precipitated with alcohol and ether. The compound, $[Y(NO_3)_4,H_2SO_4] - H_2O$, described by Sand and Genssler, could not be obtained, but by interaction of nitron sulphate with the nitrate, the *acid sulphate*, $Y_2(SO_4)_4,H_2SO_4,4H_2O$, was prepared. The *bromide*, $YBr_4,3H_2O$, is prepared by an analogous method to that used for the iodide, whilst the *acid bromide*, YBr_4,HBr,H_2O, is obtained from the acid sulphate by the action of fuming hydrobromic acid. A chloride could not be obtained. Interaction of the nitrate and oxalic acid gave the *acid oxalate*,

$$Y(C_2O_4)_2,4H_2C_2O_4,3H_2O,$$
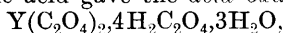
as yellowish-brown needles, which on trituration with concentrated ammonia gave the *oxalate*, $Y(C_2O_4)_2,H_2O$, as long, dark red needles. The salts $[(N_2O_2)_2Co_4(NH_3)_9H_2O](SO_4)_4,2H_2O$ and

$$[Co_3(N_2OC_2O_4)(NH_3)_9H_2O](C_2O_4H)_4$$

do not exist.

The *acid iodate*, $Y(IO_3)_4,4HIO_3$, and the *chromate*,

$$Y(CrO_4)_2,4H_2O,$$
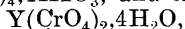
are prepared from the nitrate by treatment with iodic acid and potassium chromate respectively. The former is a dark red, crystalline powder, and the latter an amorphous, yellowish-brown salt.

The above red nitrosopentamminecobalt salts must be considered as having the general formula $(N_2O_2){<_{Co(NH_3)_5X_2}^{Co(NH_3)_5X_2}}$. Attempts to

decide the nature of the radicle N_2O_2 have not yet met with
success.   By the action of acids, the radicle is split off as $N_2O_2H_2$,
which, however, immediately decomposes, giving N_2O; the com-
pound $N_2O_2H_2$ could not be isolated or shown to be in solution,
and statements made by Sand and Genssler that it is present in
the solution obtained by the action of 68% nitric acid on the red
nitrate are not correct.   Since the compound $H_2N_2O_2$ may be
hyponitrous acid, attempts were made to synthesise the red salts
by the action of silver hyponitrite on chloropentamminecobalt
nitrate, but they were unsuccessful, aquopentamminecobalt salts
being obtained.   T. S. P.

The Solubility of some Metallic Hydroxides in Water.

GUSTAV ALMKVIST (*Zeitsch. anorg. Chem.*, 1918, **103**, 240—242).
—The solubilities of the hydroxides $Ni(OH)_2$, $Co(OH)_2$, $BiO(OH)$,
$Fe(OH)_3$, and $MnO(OH)_2$ in water at $20°$ have been determined.
As the results were required for analytical purposes, ordinary dis-
tilled water, not freed from carbon dioxide, was used.   For the
determination, the purified hydroxide was stirred for four days
with water.   About 2 litres of the filtrate were then evaporated to
a small bulk, and the quantity dissolved was estimated gravimetric-
ally, nickel and cobalt being weighed as sulphate after conversion
of the hydroxide into sulphide, bismuth as Bi_2O_3.   Iron and man-
ganese, however, were determined colorimetrically.   The following
results were obtained per litre: $Ni(OH)_2$, 12·7 mg.; $Co(OH)_2$,
3·18 mg.; $BiO(OH)$, 1·44 mg.; $Fe(OH)_3$, 0·151 mg.; $MnO(OH)_2$,
0·43 mg.   E. H. R.

New Mixed Crystals and Compounds of Nickel Oxide with other Metallic Oxides.

J. ARVID HEDVALL (*Zeitsch.
anorg. Chem.*, 1918, **103**, 249—252).—Experiments on the misci-
bility of nickel oxide with other oxides were made by fusing the
mixed oxides together in varying proportions at about $900°$, using
potassium chloride as a flux.   With magnesium oxide, homogeneous
mixed crystals are formed within the limits 27—90% nickel oxide;
outside these limits, it is difficult to distinguish microscopically
between mixed crystals and the pure oxides.   The mixed crystals
are cubic and are intermediate in colour between the components.

With zinc oxide, homogeneous mixed crystals are formed when
the zinc oxide is in excess.   The crystals appear to be hexagonal,
like those of Rinmann's Green.   Probably a nickel zincate is
formed which is miscible with excess of zinc oxide (compare A.,
1914, ii, 133; 1916, ii, 331).   The colours of mixed crystals of
varying composition are not strictly proportional to their. com-
position.

Homogeneous mixed crystals of nickel and manganese oxide
were prepared with compositions ranging from NiO,5MnO to
5NiO,MnO.   The crystals are slightly yellowish-green in colour
and form octahedra and octahedral cubes.

Nickel oxide forms with alumina a blue compound, NiO,Al_2O_3,

crystallising in small octahedra or octahedral cubes. Even a small excess of either oxide can readily be distinguished microscopically. The corresponding cobalt aluminate has been previously described (A., 1915, ii, 636).

With tin dioxide, nickel oxide reacts but slowly below 1000°, but a small quantity of a stannate analogous to cobalt stannate (A., 1915, ii, 638) appears to be formed. E. H. R.

Colloidal Products of the Reactions between Potassium Dichromate and Stannous Salts. J. C. WITT (*J. Amer. Chem. Soc.*, 1918, **40**, 1026—1030).—The phenomena observed when *N*-potassium dichromate is added to *N*-stannous chloride in equivalent proportions (Neidle and Witt, A., 1915, ii, 780; 1916, ii, 256; Neidle and Crombie, A., 1917, ii, 93) have been investigated. The mottled appearance is caused by a local excess of potassium dichromate; on keeping after the addition of an equivalent of dichromate, the remainder of the stannous chloride present gradually removed the dichromate from the precipitate, and the colloid was regenerated, producing a homogeneous, green liquid. A like precipitation of the colloids is produced by other electrolytes containing an anion having a valency greater than one. The reaction between stannous sulphate and potassium dichromate is essentially similar to that with the chloride. C. S.

Zirconium Nitride. P. BRUÈRE and ED. CHAUVENET (*Compt. rend.*, 1918, **167**, 201—203).—The authors have prepared zirconium nitride by heating the tetra-ammonia derivative of zirconium chloride, $ZrCl_4,4NH_3$, at 350°, and find that the product has the composition Zr_3N_4, and not Zr_3N_8 as given by Wöhler (compare *Annalen*, 1839, **48**, 94) or Zr_2N_3 as found by Mallet (*Amer. J. Sci.*, 1859, [ii], **28**, 346). The authors have repeated Wöhler's work, but are unable to confirm his formula. W. G.

The Combinations of Acid Zirconyl Sulphate with some Alkali Sulphates (Na, NH₄). ED. CHAUVENET and (MLLE.) H. GUEYLARD (*Compt. rend.*, 1918, **167**, 126—129. Compare this vol., ii, 269).—Thermochemical measurements indicate the existence of the following compounds of acid zirconyl sulphate with sodium sulphate and ammonium sulphate respectively:

$$2(ZrOSO_4,SO_3),3Na_2SO_4,$$
$$3(ZrOSO_4,SO_3),2Na_2SO_4,\quad ZrOSO_4,SO_3,(NH_4)_2SO_4,$$
$$ZrOSO_4,SO_3,2(NH_4)_2SO_4,$$
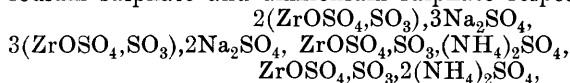
to which correspond the following hydrates, which are stable in air at the ordinary temperature: $2(ZrOSO_4,SO_3),3Na_2SO_4,8H_2O$, $3(ZrOSO_4,SO_3),2Na_2SO_4,7H_2O$, and the trihydrate in the case of each of the double ammonium salts. Measurements have been made of the density, refractive index, and electrical conductivity of solutions of mixtures of varying proportions of the acid zirconyl sulphate and one of the alkali sulphates. In the case of mixtures with potassium sulphate, the formation of a precipitate prevented the making of exact measurements. W. G.

Pure Antimony. E. GROSCHUFF (*Zeitsch. anorg. Chem.*, 1918, **103**, 164—188).—Technically refined antimony is purer than electrolytic antimony prepared by the electrolysis of antimony sulphide solutions. The latter product when further refined gives a metal of a high degree of purity, containing less than 0·02% impurity. The different methods for purifying antimony and antimony compounds are reviewed. For the production of chemically pure antimony, the following process has been adopted. Antimony trichloride or pentachloride is purified by distillation, and is then transformed into the chlorantimonic acid, $SbCl_6H,4\frac{1}{2}H_2O$, described by Weinland and Schmid (A., 1905, ii, 326). This compound is specially adapted to the separation of antimony from all likely metallic impurities. After purification by recrystallisation, the chlorantimonic acid is readily hydrolysed to antimonic acid, which is reduced to metal preferably by melting with potassium cyanide. In a large preparation (about a kilogram) purified in this way, no impurities at all could be detected by qualitative methods. The melting point of the pure antimony is 630·3°.

Methods for the qualitative and quantitative analysis of nominally pure antimony are given. The solution of the antimony is effected in a variety of ways, according to the impurities present. The antimony is then converted into chlorantimonic acid, which is fractionally crystallised. The impurities are concentrated in the mother liquors, which are combined and analysed by the usual methods. Pure antimony dissolves completely in red, fuming nitric acid without evolution of gas. Under certain conditions of precipitation, antimonic acid is obtained in a sparingly soluble modification.   E. H. R.

The Hydrates with $3H_2O$ or $n \times 3H_2O$. MARCEL DELÉPINE and PIERRE BOUSSI (*Bull. Soc. chim.*, 1918, [iv], **23**, 278—288). —A study of the dehydration of various platinichlorides, iridi- and irido-chlorides, and rhodochlorides containing 6 or $12H_2O$ does not support Rosenstiehl's views (compare A., 1911, ii, 270, 386) on polymerised water and water of crystallisation.   W. G.

The Acid Function of Osmium Tetroxide. L. TSCHUGAEV (*Compt. rend.*, 1918, **167**, 162—163).—That osmium tetroxide has an acid function is shown by the fact that it forms definite compounds with the alkali hydroxides. The *potassium* compound, $OsO_4,2KOH$, the *rubidium* compound, $OsO_4,RbOH$, and the two *cæsium* compounds, $OsO_4,CsOH$ and $2OsO_4,CsOH$, are all crystalline, of an orange or brown colour, and readily soluble in water, in which solution they are strongly hydrolysed. The *compound* $[Rh,4C_5H_5N,Cl_2]OH,2OsO_4$ was also obtained in the form of thin, yellow plates.   W. G.

Mineralogical Chemistry.

Boron, Lithium, and Thallium in Volcanic Exhalations.
A. BRUN (*Bull. Soc. franç. Min.*, 1917, **40**, 107—110).—These
elements may very often be detected spectrographically in the
saline sublimations of fumaroles and in the altered scoria of
Vesuvius and other volcanoes. Thallium was detected from
Vesuvius, Etna, and Teneriffe in amounts ranging from 2·5 to 24
in 10,000. It is present as the soluble chloride in association with
ammonium and sodium chloride, or as an insoluble sulphide in
association with sulphides of arsenic. L. J. S.

Thallium in the Lead Sulpharsenate Minerals of the Binnenthal, Switzerland. A. BRUN (*Bull. Soc. franç. Min.*, 1917,
40, 110—111).—Spectroscopic examination of crystals of sartorite,
dufrenoysite, and jordanite, as well as all fragments giving a
black or chocolate-brown streak, showed the presence of thallium.
Hutchinsonite [which contains 5% of Tl] was not detected amongst
these fragments. The association with sulphur and arsenic is here
analogous to the Vesuvian occurrence. L. J. S.

Minerals from the Stanley Antimony Mine, Idaho. EARL
V. SHANNON (*Amer. Min.*, 1918, **3**, 23—27).—The ore consists of
pure stibnite in a quartz-vein which carries some gold. The
following mineral-species are described: stibnite, blende, gold,
iron-pyrites, mispickel, kermesite, valentinite, cervantite, stibio-
ferrite, and volgerite. The volgerite occurs abundantly as an
earthy, dirty-white crust on stibnite; material from the interior of
the crusts is more compact, somewhat translucent with a faint
resinous lustre, and pale greyish-brown in colour. D^{20} 3·082, H $3\frac{1}{2}$.
The mineral is completely soluble in hot concentrated hydrochloric
acid, and at a red heat it gives off some oxygen, the higher oxide,
Sb_2O_5, apparently passing into Sb_2O_4. It contains H_2O 12·6,
Fe_2O_3 1·4%. The amount of water is lower than that required by
the usual formula ($Sb_2O_5,5H_2O$ or $Sb_2O_5,4H_2O$), but this may
perhaps be explained by the colloidal nature of the material.
L. J. S.

A peculiar Fibrous Form of Opal. GEORGE P. MERRILL
(*Amer. Min.*, 1918, **3**, 11—12).—Bunches of light grey, asbesti-
form material are embedded in a massive mixture of opal and
chalcedony from Metolius, Oregon. It has the appearance of
serpentine-asbestos (chrysotile), but is brittle and is harsh to the
touch. Under the microscope it is seen to consist of wavy, colour-
less, isotropic fibres. Analysis gave: SiO_2 89·56, $Al_2O_3 + Fe_2O_3$
4·72; loss on ignition, 5·62%. L. J. S.

16*—ᴐ

Ores of Manganese and Iron from the Crystalline Massif of Brosteni, Roumania. V. C. BUTUREANU (*Bull. Soc. franç. Min.*, 1917, **40**, 164—177).—A résumé is given of previous papers (P. Poni, A., 1901, ii, 26; Butureanu, A., 1908, ii, 955; 1909, ii, 745; 1912, ii, 949). The minerals considered are manganites of manganese and iron (brostenites of Poni) and carbonates of manganese and iron (ponites of Butureanu). The brostenites have been derived by the alteration of the ponites. Numerous analyses are quoted showing the wide range in composition.   L. J. S.

Ulexite from Lang, California. WILLIAM FOSHAG (*Amer. Min.*, 1918, **3**, 35).—This occurs in some quantity, associated with colemanite, howlite, and calcite, in the Sterling Borax Co. mine. It has a fibrous structure with a botryoidal surface; it differs from the ordinary type of this mineral in being more compact and harder ($H = 3\frac{1}{2}$) and in its association with colemanite. Analysis gave:

B_2O_3.	CaO.	H_2O.	Na_2O.	Total.
43·13	14·14	35·68	[7·05]	100·00

The mineral is probably a lake deposit from the alkaline waters of the neighbouring streams, and the colemanite has perhaps been derived from it by the action of alkaline chloride solutions.

L. J. S.

Randannite [= Diatomite] from Madagascar. A. LACROIX (*Bull. Soc. franç. Min.*, 1916, **39**, 85—88).—A bed of diatomite, interbedded with basaltic tuffs, is exposed on the banks of the stream Sandrangoty, near Mt. Raynaud, in the extreme north of Madagascar. The material is white, porous, and fairly coherent. Under the microscope, the material is seen to be colourless, colloidal, and to be composed of fusiform diatoms. Analysis by Raoult gave:

SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.
76·00	1·24	6·24	1·80	0·85	0·07	0·80

Na_2O.	K_2O.	P_2O_5.	H_2O at 105°.	H_2O (ign.).	Organic matter.	Total.
0·39	0·18	0·12	5·87	6·07	0·60	100·23

The high percentage of titanium dioxide suggests that the impurities (Al_2O_3 and SiO_2 [2·90%] insoluble in alkali) are due to the presence of admixed laterite.   L. J. S.

Lattice-like Inclusions in Calcite from North Burgess, Ontario. R. P. D. GRAHAM (*Min. Mag.*, 1918, **18**, 252—258).—Pale blue, coarsely crystalline calcite from this locality shows twin-striations, due to repeated twinning on the obtuse negative rhombohedron $e(110)$, and encloses fine needles, which are arranged parallel to the edges of this rhombohedron. On dissolving the calcite in acid, these needles remain as a delicate and intricate network or lattice-like structure. Analyses of this material, D 2·5,

gave the results under I and Ia, agreeing with the formula
5MgO,6SiO$_2$,4H$_2$O.   The material is slightly attacked by hydro-
chloric acid; after digestion with concentrated acid and drying at
100°, the residue had the composition given under II.   The blue
calcite itself (anal. III) contains very little magnesia.

	SiO$_2$.	MgO.	FeO.	CaO.	H$_2$O.	CO$_2$.	Total.
I.	57·23	30·35	1·66	0·37	n.d.	—	—
I$_A$.	56·37	30·43	2·47	nil	10·87	—	100·14
II.	63·93	26·16	1·21	—	8·08	—	99·38
III.	—	0·41	—	56·12	—	43·53	100·06

L. J. S.

Mineralogy of Black Lake Area, Quebec.   Eugene Poitevin
and R. P. D. Graham (*Museum Bull. Geol. Survey Canada*, 1918,
No. 27, 1—82).—An account is given of thirty-four mineral species
found in the several asbestos (chrysotile) and chromite mines and
quarries in the 'serpentine belt' near Black Lake, Megantic Co.,
Quebec.   Many of these minerals are alumino-silicates rich in
lime, such as idocrase, grossularite, etc., which are usually formed
by the contact-metamorphism of impure limestones.   In this area,
however, they occur as fillings in dyke-like fissures penetrating
peridotite and serpentine, that is, in rocks containing very little
lime (0·20—0·68% CaO).   These dykes are considered to represent
the last phase of the igneous intrusions, when the residual acid
magma or magmatic waters became enriched in lime by their solvent
action on the surrounding rocks.   Analyses are given of the follow-
ing minerals: I. Diopside, colourless crystals from the Montreal
chrome pit.   Corresponding with the low percentage of iron, the
refractive indices ($a_{Na} = 1·669$, $\beta = 1·676$, $\gamma = 1·698$) are lower than
any previously recorded for diopside.   II. Grossularite, colourless,
transparent crystals from Southwark pit; refractive index, 1·734.
III., lilac-coloured, and IV., yellowish-green crystals of idocrase;
the refractive indices ($\omega = 1·708$; $\epsilon = 1·705$) of the lilac-coloured
crystals are low.   V.—VII. *Colerainite*, a new species, forming
minute, colourless, hexagonal scales which are optically uniaxial
and positive ($n = 1·56$), and are often aggregated as white rosettes
or botryoidal forms.   Analysis V of the crystals leads to the
formula 4MgO,Al$_2$O$_3$,2SiO$_2$,5H$_2$O.   Analyses VI and VII are of
the underlying matrix, which is white, finely granular to compact,
and resembles unglazed porcelain in appearance; this material

	SiO$_2$.	Al$_2$O$_3$.	Fe$_2$O$_3$.	FeO.	MnO.	CaO.
I.	54·77	—	0·17	0·89	0·11	26·33
II.	39·49	22·35	—	1·00	0·15	36·62
III.	36·88	20·03	0·85	n.d.	0·23	37·61
IV.	36·62	15·96	4·30	0·54	trace	38·66
V.	24·40	22·77	0·45	n.d.	0·09	0·10
VI.	26·98	16·10	0·22	nil	0·20	0·12
VII.	33·00	13·12	—	—	—	trace
VIII.	43·31	0·38	0·27	nil	trace	0·12
IX.	50·29	6·23		1·00	—	nil
X.	48·88	3·56		1·36	—	nil

	MgO.	$(K,Na)_2O$.	H_2O.	Total.	Sp. gr.
I.	18·46	—	—	100·73	3·267
II.	0·28	—	—	99·89	3·60
III.	2·17	—	3·09	100·86	3·32
IV.	1·25	—	3·18	100·51	—
V.	32·70	0·30	19·63	100·44	2·51
VI.	36·56	0·28	19·91	100·37	2·44
VII.	35·30	0·26	18·67	100·35	2·34
VIII.	40·03	0·28	15·77	100·16	2·51
IX.	29·99	—	13·30	100·81	—
X.	31·41	—	15·67	100·88	—

consists mainly of the mineral colerainite. VIII is of ' precious ' or ' noble ' serpentine from the Megantic mine; this is chrysoprase-green and translucent with a somewhat waxy or greasy lustre. Included in it are sometimes grains and veins of chromite and the rare mineral stichtite, a chromiferous magnesium hydroxy-carbonate. IX and X are of porcellophite, an impure variety of serpentine; IX is of pale grey material from the Megantic mine, and X, of pale brown material from the Hall chrome pit; both are very compact, resembling dried clay in appearance, and so light that they float on water.   L. J. S.

Flokite, a New Zeolite from Iceland. KAREN CALLISEN (*Medd. Dansk Geol. For.*, 1917, **5**, No. 9, 1—6).—A specimen in the Copenhagen Museum, labelled 'Eskefjord? Iceland,' and regarded as mesolite, proved on examination to represent a new species. It forms slender, flattened, monoclinic prisms with perfect (100) at (010) cleavages. The crystals are water-clear or pale yellowish-green. Sections perpendicular to the prism-zone show a division into sectors with different optical orientations. $\alpha_{Na} = 1\cdot4720$, $\gamma_{Na} = 1\cdot4736$; D 2·102; H 5. Before the blowpipe, the material fuses readily with intumescence; it is not attacked by hydrochloric acid. Analysis by C. Christensen gives the formula $H_8(Ca,Na_2)Al_2Si_9O_{26},2H_2O$.

					H_2O	H_2O	
SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	> 100°.	< 100°.	Total.
67·69	12·43	2·65	0·09	4·36	8·82	4·53	100·57

L. J. S.

The Mesosiderite-Grahamite Group of Meteorites : Analysis of Vasca Muerta, Hainholz, Simondium, and Powder Mill Creek. G. T. PRIOR (*Min. Mag.*, 1918, **18**, 151—172. Compare A., 1916, ii, 635).—In the Rose-Tschermak-Brezina classification of meteorites, the mesosiderites are defined as consisting of iron and crystalline olivine and bronzite, with the metallic and stony matter in approximately equal amounts, whilst the grahamites contain the same constituents with the addition of plagioclase-felspar. It is now found that typical members of both groups contain abundant felspar, and that there is no essential difference between them. For the combined group, the earlier name mesosiderite is retained. The members of this group consist mainly of pyroxene and felspar, with nickel-iron in large amount,

but rather unevenly distributed, and nodules of olivine somewhat sparsely distributed, but occasionally of considerable size. Accessory constituents are troilite, chromite, and schreibersite. The felspar is nearly pure anorthite; the pyroxene is fairly rich in iron, the ratio of MgO:FeO being about 2:1; the olivine, on the other hand, is poor in iron, the ratio MgO:FeO being from 6:1 to 10:1; and the nickel-iron is poor in nickel, Fe:Ni=10:1 to 13:1. The cataclastic structure of the mesosiderites suggests that they represent a mixture of two types, to one of which belong the pyroxene and anorthite, and to the other the iron and olivine.

Vaca Muerta (Chili).—Several masses (' Sierra de Choca,' 'Llano del Inca,' 'Doña Inez,' etc.) are included in this fall. The bulk-composition (I) is deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the unattracted portion. Ia is of the olivine, corresponding with $10Mg_2SiO_4,Fe_2SiO_4$, and Ib is the mineral composition. Hainholz (Westphalia).—II the bulk-composition, IIa of the olivine ($7Mg_2SiO_4,Fe_2SiO_4$), and IIb the mineral composition. Simondium (Cape Colony) (A., 1910, ii, 315).—This is much weathered. The portion of the unattracted material soluble in water contained NiO 1·28, CaO 0·91, SO$_3$ 2·71%. Other detailed analyses are given. Powder Mill Creek (Tennessee).—The attracted portion contained Fe 73·15, Ni 5·61, insoluble 11·58, anorthite, etc. (9·66)=100. The olivine gave IIIa, corresponding with $10Mg_2SiO_4,Fe_2SiO_4$. The composition of some other meteorites of this group is also discussed.

Nickel-iron.			Troilite.		Schreibersite.						
Fe.	Ni.	Co.	Fe.	S.	Fe.	Ni.	P.	SiO$_2$.	Al$_2$O$_3$	Fe$_2$O$_3$.	Cr$_2$O$_3$.
I. 38·25	2·90	0·36	1·37	0·79	1·27	0·70	0·35	26·02	5·87	1·36	0·45
II. 42·13	4·00	0·41	2·52	1·44	0·36	0·23	0·10	21·69	4·99	2·77	0·33

FeO.	MnO.	NiO.	CaO.	MgO.	Na$_2$O.	P$_2$O$_5$.	H$_2$O.	Total.
I. 7·03	0·24	—	4·35	7·36	0·18	—	0·54	99·39
II. 6·19	trace	0·48	3·49	7·07	0·21	0·34	1·20	99·95

	SiO$_2$.	FeO.	MgO.	Insol.	Total.
I$_A$.	39·89	8·98	49·50	1·95	100·32
II$_A$.	40·48	11·59	42·97	2·76	97·80
III$_A$.	40·18	9·15	48·91	1·42	99·66

	Nickel-iron.	Troilite.	Anorthite.	Pyroxene.
I$_B$.	41½	2	17	32
II$_B$.	46½	4	14½	27

	Olivine.	Chromite.	Rust.	Schreibersite.
I$_B$.	1½	1	2	3
II$_B$.	1½	½	4	2

L. J. S.

Composition of the Meteorites Amana and Eagle Station.

G. T. PRIOR (*Min. Mag.*, 1918, **18**, 173—179).—The Amana or Homestead meteoric stones, which fell in Iowa Co., Iowa, on

February 12th, 1875, were in the same year analysed by G. D. Hinrichs, J. L. Smith, and by C. W. Gümbel and Schwager. These analytical results show some discrepancies amongst themselves and are not in agreement with the author's theory of the genetic relationship of meteorites (A., 1916, ii, 635). The following new analysis was therefore made. The bulk-composition (I) deduced from analyses of the magnetically attracted portion and of the portions soluble and insoluble in hydrochloric acid of the unattracted portion, agrees with the following mineral composition: felspar 9·76, apatite 0·22, chromite 0·44, bronzite

$$(4\tfrac{1}{2}MgSiO_3,FeSiO_3,\tfrac{1}{2}CaSiO_3)$$
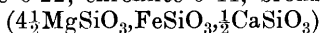
30·75, olivine $(3\tfrac{1}{2}Mg_2SiO_4,Fe_2SiO_4)$ 40·15, nickel-iron 10·99, troilite 6·25, water 0·47%. This meteorite therefore contains about 11% of nickel-iron in which the ratio of Fe : Ni is 8 : 1, whilst the ratio of MgO : FeO in the ferromagnesian silicates is 4 : 1; it thus occupies an intermediate position between the type-meteorites Cronstad (C2) and Baroti (C3).

Nickel-iron.

	Fe.	Ni.	Co.	Fe.	S.	SiO$_2$.	Al$_2$O$_4$.	Cr$_2$O$_3$.	Fe$_2$O$_3$.
I.	9·71	1·19	0·09	3·97	2·28	39·27	2·10	0·32	0·40

	FeO.	MnO.	CaO.	MgO.	Na$_2$O.	K$_2$O.	H$_2$O.	P$_2$O$_5$.	Total.
I.	12·06	0·08	1·78	24·88	0·92	0·13	0·47	0·26	99·91

A new analysis of the Eagle Station meteorite, which was found in 1880 in Carroll Co., Kentucky, gave II for the attracted portion and III for the olivine. These results confirm those of J. B. Mackintosh (1887). In the nickel-iron the ratio of Fe : Ni is about 6 : 1 (instead of more than 10 : 1, as in most other pallasites), and in the olivine the ratio of MgO : FeO is about 4 : 1 (instead of about 7 : 1). In composition, as well as in structure, this pallasite is thus exceptional; and it may perhaps be placed in the group A3 (A., 1916, ii, 635).

	Fe.	Ni.	Co.	SiO$_2$.	MgO.	FeO.	P,S,&c.	Total.
II.	79·74	13·98	1·04	1·42	1·74	0·77	(1·31)	100·00
III.	—	—	—	39·22	42·31	18·83	—	100·36

L. J. S.

Analytical Chemistry.

Quinone–Phenolate Theory of Indicators. Absorption Spectra of Solutions of Phenolsulphonephthalein and its Tetrabromo- and Tetranitro-derivatives and their Salts, and of Analogous Substances. E. C. WHITE and S. F. ACREE (*J. Amer. Chem. Soc.*, 1918, **40**, 1092—1099).—Since phenol-sulphonephthalein and its derivatives and their salts furnish the best series of indicators yet found for acidimetry and for the study

of the quinone–phenolate theory (White, *Science*, 1915, **42**, 101; Lubs and Acree, A., 1917, ii, 97; Lubs and Clark, A., 1916, ii, 44, 570; White and Acree, A., 1917, i, 340), the authors intend to make a series of phenolsulphonethaleins covering a range of hydrogen-ion concentrations from 10^{-1} to 10^{-13} or more.

The following results are established in the present paper. The yellow colour and the absorption spectrum of phenolsulphone-phthalein solutions are not altered by the addition of alkali hydroxide up to 0·75 mol. When more alkali is added, the yellow colour changes to deep red, and there is a corresponding shift in the absorption band. This is interpreted as evidence that the intense red colour of the alkali salts of indicators of this series does not come from the non-ionised quinone–phenol group, but arises from the quinone–phenolate anion. In accordance with this conception, it is found that the introduction of negative bromo- and nitro-groups into the phenol nucleus increases the ionisation of the phenol group, increases the conductivity, lowers the P_H value, and gives to the solution a greater concentration of quinone–phenolate anions, and therefore increases the deep red colour and changes the position of the absorption band so as to cut out a part of the yellow. The addition of hydrochloric acid suppresses the ionisation of the phenol group and changes the deep red colour into the yellow of the quinone, and therefore shifts the absorption band so as to include less of the yellow.

The similarity of the absorption spectra of alkaline solutions of sulphonephthaleins, phenolphthaleins, aurin, fluorescein, and related substances gives evidence that the deep red colour in all these cases arises from the presence of a quinone–phenolate anion.

C. S.

Behaviour and Detection of the smallest Quantities of Carbon Monoxide in the Chlorate Pipette. K. A. HOFMANN and HELGE SCHIBSTED (*Ber.*, 1918, **51**, 837—842. Compare A., 1916, ii, 636, 637).—It has already been emphasised that the rate at which hydrogen is absorbed in the " chlorate pipette" (sodium chlorate solution activated by osmium tetroxide; porous rods impregnated with platinum and a little palladium) is greatly lessened by traces of carbon monoxide. In order to render this influence most obvious, it is not advisable to consider the observed rate of absorption, for this depends on the surface area of the platinised tubes which reach out into the gas, and these become more and more immersed in the chlorate solution as the oxidation proceeds. The exposed surface is obviously proportional to the volume of gas left unabsorbed, for the tubes are arranged vertically in a cylindrical part of the apparatus, and therefore it is possible to arrive at the "relative rate of absorption." With pure hydrogen, this relative rate is constant, or slowly rises, until half the gas is absorbed, whilst traces of carbon monoxide cause a rapid fall in this rate. If the pipette is standardised and a curve is plotted connecting the relative rates of absorption at " half

volume " with various proportions of carbon monoxide, the pheno-
menon can be employed further for quantitative purposes.

<div align="right">J. C. W.</div>

Estimation of Chlorine in Urine. EMIL VOTOČEK (*Chem.
Zeit.*, 1918, **42**, 317—318).—Ten c.c. of the urine are diluted with
water to about 160 c.c., 5 c.c. of nitric acid and 6 drops of sodium
nitroprusside solution (0·6 gram of the salt in 3 c.c. of water) are
added, and the mixture is titrated with $N/10$-mercuric nitrate
solution until a turbidity develops; the turbidity, when the end-
point is reached, should not disappear within less than two minutes.

<div align="right">W. P. S.</div>

**Detection and Estimation of Bromine, especially in
Mineral Waters.** JOSÉ CASARES and A. TASTET (*Anal. Fis. Quim.*,
1918, **16**, 226—228).—A modification of Guareschi's method of
estimating bromine (A., 1912, ii, 1208) which enables 0·0002 gram
of bromine per litre to be detected.

<div align="right">A. J. W.</div>

Volumetric Estimation of Sulphur in Pyrites and Slag.
ERNEST MARTIN (*Mon. Sci.*, 1918, [v], **8**, ii, 149—150).—The slag
or pyrites is treated with aqua regia, the solution evaporated to
dryness, and the residue redissolved in dilute hydrochloric acid.
The solution is diluted, and sodium carbonate added. The assay
may also be opened out by fusion with sodium peroxide or a mixture
of sodium carbonate and potassium nitrate, dissolved in water, and
carbon dioxide passed through to precipitate lead. After filtration,
methyl-orange is added, and the solution exactly neutralised with
hydrochloric acid. The carbon dioxide is boiled off, and to the
luke-warm solution a known volume of standard barium hydr-
oxide and phenolphthalein are added. Carbon dioxide is bubbled
through until the colour just changes, when the solution is cooled
and titrated with $N/2$-hydrochloric acid.

<div align="right">F. C. T.</div>

**Estimation of Thiosulphuric, Sulphurous, Trithionic, and
Sulphuric Acids in a Mixture.** O. BILLETER and B. WAVRE
(*Helvetica Chim. Acta*, 1918, **1**, 174—180).—The authors describe
methods by which the above-named acids may be estimated in a
mixture of all four. The total sulphur present is oxidised to
sulphuric acid by warming with bromine water and the whole
estimated as barium sulphate. The sum of the sulphite and thio-
sulphate is next estimated by titration with a standard iodine
solution. The sulphite is then estimated alone by titration with a
solution of sodium disulphide, according to the equation $Na_2S_2 +
Na_2SO_3 = Na_2S + Na_2S_2O_3$.

The estimation is carried out in the presence of ammonium
chloride at the boiling point, the end of the reaction being indicated
by the persistence of the yellow colour of the standard solution.
It is also advisable to circulate a current of carbon dioxide over
the solution during titration.

Sodium trithionate reacts with sodium sulphide according to the equation $Na_2S + Na_2S_3O_6 = 2Na_2S_2O_3$, and consequently can then be estimated by a further titration with standard iodine. The reaction is carried out by boiling the solution with sodium sulphide for a few minutes, then adding sodium acetate and acetic acid and boiling to decompose excess of sulphide, and finally titrating with iodine. Should sulphite also be present, the thiosulphate titrated here will be made up (1) of that produced from the sulphite and (2) that produced from the trithionate, but as the amount due to the sulphite estimation is known, the calculation of the concentration of the trithionate follows. The method is very good, and in the estimation of the sulphite the end-point is emphasised by the appearance of a turbidity due to the liberation of sulphur. The amount of trithionate may be estimated by two other methods. (1) After the sulphite and thiosulphate have been titrated with iodine, sodium iodide is added and an excess of iodine, and the mixture heated under pressure; this oxidises the trithionate to sulphate. The same action occurs with the tetrathionate formed in the first estimation, and allowance must be made for this. After boiling for a few minutes, the flask is cooled and the excess iodine titrated with thiosulphate. (2) This method is based on the decomposition by trithionic acid according to the equation $H_2S_3O_6 = H_2SO_4 + SO_2 + S$. The mixture is acidified, and boiled while a current of carbon dioxide is passed through until all the sulphur dioxide has been expelled; the free sulphur is then filtered off and the sulphate estimated with barium chloride. This sulphate will represent 97·9—97·5% of the trithionate, and, of course, contains the sulphate originally present.   J. F. S.

[**Analysis of Organo-selenium Compounds.**] FRITZ VON KONEK and OSKAR SCHLEIFER (*Ber.*, 1918, **51**, 852—855).—See this vol., i, 407.

Micro-Dumas Estimation of Nitrogen in Liquids Poor in Nitrogen. GEORG KRAEMER (*J. pr. Chem.*, 1918, [ii], **97**, 59—60).— The micro-Kjeldahl method for estimating nitrogen in small quantities of liquids such as milk can be replaced satisfactorily by a micro-Dumas process working with approximately 0·25 c.c. [See also *J. Soc. Chem. Ind.*, 526A.]   D. F. T.

The Estimation of Nitrogen by the Kjeldahl Method. A. VILLIERS and (MLLE.) A. MOREAU-TALON (*Bull. Soc. chim.*, 1918, [iv], **23**, 308—311).—The authors advocate the combination of the method in which potassium sulphate is used with that in which mercury is used. The substance is digested with potassium sulphate and sulphuric acid until colourless, and, after partial cooling, 1 gram of mercury is added, and the digestion is continued for a quarter of an hour after the mixture has boiled. The remainder of the estimation is carried out as usual.   W. G.

The Estimation of Ammonia and Hydrochloric Acid by Weighing as Ammonium Chloride. A. VILLIERS (*Bull. Soc. chim.*, 1918, [iv], **23**, 306—308).—The author reaffirms the accuracy of his method (compare A., 1900, ii, 310) for the estimation of ammonia or hydrochloric acid by weighing as ammonium chloride.   W. G.

Estimation of Ammonia in Urine, Serum, etc. H. WIESSMANN (*Landw. Versuchs.-Stat.*, 1918, **91**, 346—352).—Distillation in the presence of dilute sodium carbonate solution at 50° and under 5 to 10 mm. pressure is recommended; urea does not yield any ammonia under these conditions. [See, further, *J. Soc. Chem. Ind.*, 532A.]   W. P. S.

Estimation of Nitrates and Nitrites. WILHELM STRECKER (*Ber.*, 1918, **51**, 997—1004).—Two well-known reactions are employed for the estimation of nitrites and nitrates in mixtures, namely, those represented by the equations $NO_2' + NH_4^{\cdot} = N_2 + 2H_2O$ and $NO_3' + 3Fe^{\cdot\cdot} + 4H^{\cdot} = NO + 3Fe^{\cdot\cdot\cdot} + 2H_2O$. The solution to be analysed, containing nitrites and nitrates equivalent to not more than 0·11 gram $NaNO_2$ and 0·18 gram KNO_3, is dropped into a boiling, concentrated solution of ammonium chloride, at least 100 times as much of this salt being taken as the nitrite present, the solution being in a flask which is provided with an apparatus for producing air-free carbon dioxide on the one hand, and a water-cooled Schiff's nitrometer containing potassium hydroxide on the other. After adjusting the pressure and noting the volume of nitrogen, a solution of iron in concentrated hydrochloric acid is introduced and the nitric oxide collected.

The process and apparatus are minutely described, but contain no novel features.   J. C. W.

The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. III. The Compound Magnesium Tetra-ammonium Diphosphate. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **103**, 73—78. Compare this vol., ii, 266).—The presence in solution of a large quantity of ammonium chloride when magnesium ammonium phosphate is precipitated affects the purity of the precipitate and the accuracy of the result, which is low if the magnesium chloride is added to the phosphate solution, high if precipitation is carried out the reverse way. The presence of an excess of ammonium ions is likely to favour the formation of the compound $Mg[(NH_4)_2PO_4]_2$, but attempts to isolate this substance have failed. The precipitate of magnesium ammonium phosphate obtained from a solution saturated with ammonium chloride is found to be partly insoluble in hydrochloric acid after calcination, the insoluble portion being magnesium metaphosphate, and amounting to 10—17% of the weight of the calcined precipitate. Experiments show that the metaphosphate decomposes slowly when heated with a blast flame, more quickly, however, than the pyrophosphate.

The metaphosphate is probably not formed by the direct decomposition $Mg[(NH_4)_2PO_4]_2 = Mg(PO_3)_2 + 2NH_3 + 4H_2O$. There is always a certain loss of phosphoric acid, which can be accounted for by the decomposition of magnesium tetra-ammonium diphosphate according to the equation $Mg[(NH_4)_2PO_4]_2 = MgNH_4PO_4 + (NH_4)_3PO_4$. The ammonium phosphate dissociates on heating, part of the phosphoric acid being volatilised, part reacting with pyrophosphate to form metaphosphate. E. H. R.

The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. A. VILLIERS (*Bull. Soc. chim.* 1918, [iv], **23**, 305—306).—The author considers that his method (compare A., 1893, ii, 434), in which the phosphate is precipitated as ammonium phosphomolybdate and weighed as such under definite conditions, is more accurate than that of Clarens (compare this vol., ii, 128). W. G.

A New Method of Qualitative Analysis without the Use of Hydrogen Sulphide. GUSTAV ALMKVIST (*Zeitsch. anorg. Chem.*, 1918, **103**, 221—239).—The new method, which is described in detail, can be outlined as follows. The sample is first brought into solution, using aqua regia if necessary, but any residue insoluble in aqua regia need not be filtered off. Potassium hydroxide is added to the solution until its strength is about N, followed by potassium carbonate and hydrogen peroxide, the last to destroy oxalic acid and bring chromium into solution. The metals remaining in solution, forming Group I, are arsenic, antimony, tin, lead, zinc, aluminium, and chromium. All other commoner metals are precipitated, forming Group II, except sodium, potassium, and ammonium, which form Group III.

The solution containing Group I is divided into two parts. One part is reduced with iron and hydrochloric acid, whereby arsenic and antimony are reduced to metal, and eventually to their hydrides, which are identified by distillation, tin to stannous chloride. The second part of the solution is treated with sodium sulphide solution in excess, lead and zinc being precipitated as sulphides, chromium as hydroxide, aluminium remaining in solution as aluminate. The aluminium is precipitated as carbonate by a stream of carbon dioxide, the other elements of the group being identified by usual tests.

The precipitate containing the elements of Group II is dissolved by treatment with nitric acid and hydrogen peroxide. The insoluble portion, including that part of the sample originally insoluble in aqua regia, is worked up by usual methods. The solution is treated with freshly precipitated stannic hydroxide and evaporated to dryness to precipitate silicic, phosphoric, arsenic, and antimonic acids, and again extracted with nitric acid. The acid solution is then made strongly alkaline and boiled with hydrogen peroxide to precipitate iron, bismuth, and manganese, then ammonium oxalate added to precipitate calcium, strontium,

and barium. The combined precipitates are evaporated with acetic acid, when calcium, strontium, and barium dissolve as acetates, iron, bismuth, and manganese being undissolved. The individual elements are identified by usual tests.

The filtrate from the iron–barium precipitates contains silver, mercury, copper, cadmium, nickel, cobalt, and magnesium. Silver and mercury are precipitated as metal by means of hydrazine sulphate, copper as cuprous thiocyanate, and the remaining metals detected by special tests.

The method does not claim to effect complete separations of the different groups, but it is efficient for the qualitative detection of the common elements. The modifications of procedure necessary when acid radicles are present which may lead to the formation of complex metallic compounds are described in detail.   E. H. R.

Sulphide Precipitation of Group 2a Metals. JOSEPH SHIBKO (*Chem. News*, 1918, **117**, 253—254).—When these metals are precipitated from a slightly acid solution of a brass or bronze by ammonium sulphide instead of hydrogen sulphide, the precipitate contains small quantities of zinc. [See also *J. Soc. Chem. Ind.*, 517A.]   C. S.

Petersen's Method for the Qualitative Separation of the Cations of the so-called Third and Fourth Groups. IWAN BOLIN and GUNNAR STARCK (*Zeitsch. anorg. Chem.*, 1918, **103**, 69—72).—A number of modifications of Petersen's process (A., 1910, ii, 654) are suggested. After precipitating the metals of the second group with hydrogen sulphide, Petersen precipitates strontium and barium with sulphuric acid. Instead, the authors use sodium sulphate. The precipitate is washed with hot water and the washings are tested for calcium with ammonium oxalate. The residue is then ignited with a little pure carbon, dissolved in 4N-acetic acid and examined for barium and strontium in the usual way. The authors prefer reduction with carbon to fusion with sodium carbonate.

In the separation of chromium from a mixture of iron, manganese, chromium, calcium, and magnesium hydroxides, it is better to oxidise the chromium to chromate with sodium hypochlorite. When sodium peroxide is used, it cannot be completely washed from the residue, and on acidification the hydrogen peroxide formed reduces manganese dioxide, and the manganese, passing into solution with calcium and magnesium, is precipitated with the latter.

For detecting zinc in the group of metals precipitated by sodium sulphide, the precipitate is boiled with alkaline sodium hypochlorite, zinc and chromium passing into solution. The solution is acidified with acetic acid, the chromate precipitated with barium chloride, and the filtrate tested for zinc with ammonium sulphide.

In presence of oxalic acid, the test for aluminium always fails.

Oxalic acid, if present, should be destroyed by boiling with 3% hydrogen peroxide and sulphuric acid. The Petersen process, with these modifications, gives very satisfactory results. E. H. R.

Estimation of Magnesia in Water. M. MONHAUPT (*Chem. Zeit.*, 1918, **42**, 338).—The water is neutralised, using methylorange as indicator, treated with a quantity of potassium oxalate slightly in excess of the amount of calcium oxide in the water, and a definite excess of $N/10$-alkali solution (prepared by mixing equal volumes of $N/10$-sodium hydroxide and sodium carbonate solutions) is added; the solution is diluted to a definite volume, filtered, an aliquot portion of the filtrate treated with a quantity of calcium chloride equivalent to the oxalate added, and the excess of alkali then titrated with $N/10$-acid. W. P. S.

Gravimetric and Volumetric Determination of Zinc Precipitated as Zinc Mercury Thiocyanate. GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1918, **40**, 1036—1039).—Lundell and Bee's method of estimating zinc in alloys as zinc mercury thiocyanate (*Trans. Amer. Inst. Met.*, 1914, 146) is subjected to criticism, the more important being: (1) arsenious compounds need not be removed, and (2) the factor for obtaining the weight of zinc is 0·13115, not 0·1266, since the precipitate, after being dried at 102—108°, has the composition $ZnHg(SCN)_4$, not
$$ZnHg(SCN)_4,H_2O.$$
Instead of weighing the zinc mercury thiocyanate, a trustworthy volumetric method of estimating the zinc in it is described, based on the reaction $ZnHg(SCN)_4 + 6KIO_3 + 12HCl = ZnSO_4 + HgSO_4 + 2H_2SO_4 + 4HCN + 6ICl + 6KCl + 2H_2O.$ C. S.

A New Reaction of Osmium. L. TSCHUGAEV (*Compt. rend.*, 1918, **167**, 235).—When a solution containing osmium in the form of its tetroxide or as an osmichloride is warmed for a few minutes with thiocarbamide in excess and a few drops of hydrochloric acid, the liquid becomes coloured a deep red or a rose colour, according to the concentration of the osmium. By this means, osmium may be detected at a dilution of 1 in 100,000. The red *compound* has the composition $[Os,6CS(NH_2)_2]Cl_3,H_2O$, and is thus analogous to the luteo-cobalt salts. W. G.

New Method for the Rapid Destruction of Organic Matter. PAUL DURET (*Compt. rend.*, 1918, **167**, 129—130).—The method consists in boiling the material with 10% sulphuric acid and ammonium persulphate until all brown coloration has disappeared, repeated additions of ammonium persulphate being made if necessary. The method is applicable to urines, hair, wool, and also to such substances as sugars, fats, glycerol, and cacodyl compounds. W. G.

Pregl's Microanalytical Estimation of Methyl Groups attached to Nitrogen. S. EDLBACHER (*Zeitsch. physiol. Chem.*, 1918, **101**, 278—287).—An account of the difficulties encountered in carrying out Pregl's method, and of various improvements by means of which they have been overcome, the principal being the adoption of a quartz flask instead of one of glass and the addition of a catalyst, gold chloride, which so accelerates the cleavage of the alkyl groups that the whole operation can be completed in one distillation occupying about thirty minutes.   H. W. B.

Reaction of Guaiacol Carbonate. A Test for Ethyl Ether. G. MAUE (*Pharm. Zeit.*, 1918, **63**, 255—256).—To identify the presence of guaiacol in guaiacol carbonate, 0·02 gram of the latter is dissolved in 1 c.c. of alcohol, 2 drops of ferric chloride solution and 1 drop of formaldehyde solution are added, and 2 c.c. of sulphuric acid are then run in so as to form a layer under the mixture. A cherry-red ring develops at the junction of the two liquids. The test may be used for the detection of aldehydes in ethyl ether; although aldehydes other than formaldehyde do enter into the reaction, the author has found that the aldehydes which may be present in ethyl ether always include some formaldehyde. One c.c. of the ether is mixed with 0·02 gram of guaiacol carbonate, 1 c.c. of water and 1 drop of ferric chloride solution, and 2 c.c. of sulphuric acid are added. Pure ethyl ether for anæsthetic uses should not yield a red-coloured zone (absence of aldehydes); ordinary ether usually gives a reaction with the test. The sensitiveness of the test is 1 in 300,000.   W. P. S.

Estimation of Cholesterol in Blood Serum. ADOLPH BERNHARD (*J. Biol. Chem.*, 1918, **35**, 15—18. Compare Weston, A., 1917, ii, 156).—The new method combines the extraction method of Weston and Kent and the colorimetric method of Grigaut (*Compt. rend. Soc. Biol.*, 1910, **68**, 827). The cholesterol is extracted by a mixture of alcohol and ether (1:1), and an estimation can be completed in five hours.   H. W. B.

Cleavage of Digitonincholesteride. A. WINDAUS (*Zeitsch. physiol. Chem.*, 1918, **101**, 276—277. Compare Lifschütz, this vol., ii, 179).—The author gives further details of his method for the preparation of cholesteryl acetate from digitonincholesteride, but points out that the cleavage is more readily accomplished by the action of hot xylene (Windaus, A., 1910, ii, 462) or by one of the more recent methods, involving the use of acetic anhydride (see Prescher, A., 1917, ii, 275).   H. W. B.

Rate of Production of Colour in Alkaline Solutions of Dextrose and Picrate. T. ADDIS and A. E. SHEVKY (*J. Biol. Chem.*, 1918, **35**, 43—51. Compare this vol., ii, 247).—A full account of work previously published.   H. W. B.

Modification of the Picrate Method for the Estimation of Dextrose in Blood. T. ADDIS and A. E. SHEVKY (*J. Biol. Chem.*, 1918, **35**, 53—59).—The chief modification consists of the utilisation of a graph showing the increase of intensity of colour corresponding with increase in the concentration of dextrose for correcting the values for the dextrose in blood obtained by the picrate method of estimation.　　　　　　　　　H. W. B.

Estimation of Dextrose by [Sodium] Hypoiodite. RICHARD WILLSTÄTTER and GUSTAV SCHUDEL (*Ber.*, 1918, **51**, 780—781).—The dextrose solution is mixed with about twice the amount of $0.1N$-iodine solution necessary for oxidation to gluconic acid, a quantity of $0.1N$-sodium hydroxide which is 1.5 times as much as the iodine is slowly added, the mixture is left for twelve to fifteen minutes (or twenty minutes if the proportion of sugar is very small), and then the excess of iodine is titrated after slightly acidifying with sulphuric acid. Taking 10 c.c. of sugar solution, the average error is less than 0.1% with 1% solutions, or less than 1.5% with 0.1% solutions.

Under these conditions, ketoses and sucrose are not affected, and therefore the method will be very useful in the estimation of aldoses in mixtures. The fundamental reaction is expressed thus:

$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CHO + I_2 + 3NaOH =$$
$$OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CO_2Na + 2NaI + 2H_2O.$$
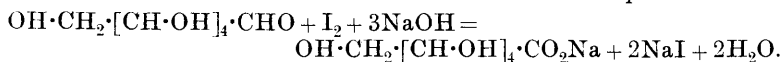
　　　　　　　　　　　　　　　　　　　　J. C. W.

Detection of Sugar in Urine by means of an Alkaline Copper Solution. H. RUOSS (*Zeitsch. physiol. Chem.*, 1918, **101**, 193—209).—A modification of the Worm-Müller test is described in which the quantity of the alkaline copper reagent to be boiled with 5 c.c. of the urine depends on the density of the urine. The number of c.c. of reagent required is determined by the formula $83(D-1) + 0.7$, where D is the density of the urine. If a deposit of red cuprous oxide fails to form when the calculated volume of the reagent is mixed with 5 c.c. of urine under the prescribed conditions of temperature and dilution, the urine is normal. By the addition of glycerol to the reagent, its delicacy is greatly increased, so that the presence of dextrose may be detected in even normal urines.　　　　　　　H. W. B.

Estimation of Lactose in Admixture with Sucrose and Invert-sugar. J. GROSSFELD (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 249—256).—The following formulæ, deduced from the results obtained by experiments with the pure sugars, are given for calculating the quantity of lactose in a mixture also containing sucrose and invert-sugar. The mixed sugars are inverted by heating 50 c.c. of their solution at $100°$ for thirty minutes with 2 c.c. of hydrochloric acid (D 1.125), and the optical rotation and reducing power of the solution are then determined, the rotation being observed after the solution has remained for twenty-four hours.

Lactose $= 0\cdot01375Z(D + 16\cdot7)$ and sucrose $= 0\cdot01145Z(70\cdot6 - D)$, where Z is the total reducing sugar (as invert-sugar) and D its specific rotation.   W. P. S.

Detection of Methylpentosans. KINTARO ŌSHIMA and KINSUKE KONDŌ (*J. Tokyo Chem. Soc.*, 1918, **39**, 185—198).—Methylpentosans frequently occur together with pentosans in vegetable substances.   In such a case, Ōshima and Tollens's method (A., 1901, ii, 484) for detecting methylpentosans is the most sensitive. If other hydrocarbons of the hexose group are present in addition to methylpentosans and pentosans, the spectroscopic determination of methylfurfuraldehyde in Ōshima and Tollens's method needs some skill, as hydroxymethylfurfuraldehyde derived from hexose will also be found, and its absorption spectrum closely resembles that of methylfurfuraldehyde.   The authors describe an improved method depending on the fact that hydroxymethylfurfuraldehyde can be destroyed completely by distillation with hydrochloric acid. Three to five grams of the sample are distilled according to Kröber and Tollens's method (compare A., 1902, ii, 288, 537).   When the volume of the distillate reaches 300 c.c., 100 c.c. of it are taken and subjected to a second distillation.   When 30 c.c. of liquid have distilled, an equal amount of the first distillate is run into the distilling flask by means of a separating funnel.   This procedure is repeated until the whole of the first distillate has been added; the distillation is then continued with additions of hydrochloric acid (D 1·06) in the same manner until the total volume of distillate amounts to 400 c.c.   To 5 c.c. of the second distillate, an equal volume of concentrated hydrochloric acid is added, and then a small quantity of a solution of phloroglucinol in hydrochloric acid (D 1·06).   After five minutes or more, the precipitate of phloroglucide is filtered off and the absorption band of methylfurfuraldehyde determined in the filtrate.   S. H.

Sudan III. and the Detection of Fat. V. H. MOTTRAM (*Proc. Physiol. Soc.*, 1918, xviii—xix, *J. Physiol.*, **52**; from *Physiol. Abstr.*, 1918, **3**, 162—163).—For the detection of fat in physiological mixtures, 1 gram of the powdered solid is shaken with 10 c.c. of a saturated solution of Sudan III in 70% alcohol. The colour of the filtrate is compared with that of the control (1 gram of fat-free starch, etc., similarly treated).   If the filtrate is markedly lighter in colour, more than 0·04% of fat is present. For the detection of fat in milk, the curd is treated with acetic acid and filtered; the contents of the filter are treated as above.
                                                             S. B. S.

Estimation of Anthraquinone. HARRY F. LEWIS (*J. Ind. Eng. Chem.*, 1918, **10**, 425—426).—Anthraquinone mixed with large amounts of anthracene or phenanthraquinone may be estimated by boiling the mixture with an excess of 5% sodium

hydroxide solution and zinc dust; the reduction product is soluble in alkaline solution, and is separated from the insoluble substance by filtration. Re-oxidation occurs when the filtrate is shaken with air, and the resulting anthraquinone is then collected, dried, and weighed. W. P. S.

Analysis of Commercial "Saccharin." Estimation of o-Benzoylsulphonimide from the Ammonia Produced by Acid Hydrolysis. H. DROOP RICHMOND and CHARLES ALFRED HILL (*J. Soc. Chem. Ind.*, 1918, **37**, 246—249T).—The various methods available for the analysis of "saccharin" are criticised. It is shown that Reid's hydrochloric acid method (A., 1899, ii, 581) is accurate but rather troublesome. Proctor's method (T., 1905, **87**, 242) tends to low results; it is insufficiently described and leads to discrepancies between analyses. By increasing the time of hydrolysis to four hours or the strength of the acid to $1.5N$, it becomes trustworthy. The following method is recommended. The "saccharin" is boiled for two minutes with 10 c.c. of $7.5N$-sodium hydroxide to expel free ammonia, and then for fifty minutes with 15 c.c. of $10N$-hydrochloric acid, using an efficient reflux condenser. The liquid is cooled and 75 c.c. of cold water are added; 15 c.c. of $7.5N$-sodium hydroxide are added, and the ammonia is distilled into 20 c.c. of $0.2N$-hydrochloric acid. The excess of acid is then titrated with $0.1N$-alkali, using methyl-red as indicator. J. F. S.

Identification of the Cinchona Alkaloids by Optical-crystallographic Measurements. EDGAR T. WHERRY and ELIAS YANOVSKY (*J. Amer. Chem. Soc.*, 1918, **40**, 1063—1074).—Cinchonine, cinchonidine, quinine, and quinidine are separately crystallised from alcohol or benzene, and the crystals are optically examined under the microscope in ordinary light and in parallel and in convergent polarised light; the refractive indices are measured by the immersion method in solutions of potassium mercuric iodide and glycerol of known indices. Tables of the data thus obtained are given. It is shown that the individual alkaloids in a mixture of the four can be identified by the data, and a description is given of the application of the method to the identification of the alkaloids in a medicinal preparation. [See *J. Soc. Chem. Ind.*, 529A.] C. S.

Colorimetric Estimation of Brucine in Presence of Strychnine. A. WÖBER (*Zeitsch. angew. Chem.*, 1918, **31**, i, 124). —The drawback of Dowzard's colorimetric method of estimating brucine in presence of strychnine (P., 1902, **18**, 220) is that the coloration fades with varying velocity according to the concentration of the alkaloid solution. The strong nitric acid used for the reaction also affects the strychnine, producing a yellow coloration. The method may be rendered trustworthy by using a mixture of equal volumes of strong nitric acid (D 1.4) and 20% sulphuric

acid as the reagent, and adding a small amount of a saturated aqueous solution of potassium chlorate immediately after the reaction. The standard brucine solution used for the comparison should contain 0·1 gram of strychnine. [See also *J. Soc. Chem. Ind.*, 441A.]   C. A. M.

Extraction of Nicotine from Aqueous Solutions. KARL DANGELMAJER (*Chem. Zeit.*, 1918, **42**, 290).—Trichloroethylene is a useful solvent for extracting nicotine from its alkaline aqueous solution; the extraction is quantitative, and the nicotine may be recovered from the trichloroethylene solution by shaking the latter with dilute sulphuric acid.   W. P. S.

Identification of Novocaine. J. A. SANCHEZ (*Rev. farm. Buenos-Ayres*, 1917, 699; from *Ann. Chim. anal.*, 1918, **23**, 137). —A red coloration is obtained when a 0·2% novocaine solution is heated with 2 drops of 10% sodium nitrite solution and 3 drops of sulphuric acid, then diluted with water and treated with Millon's reagent. This reaction identifies the phenolic nucleus of the substance. The ethylic nucleus is identified by the formation of iodoform, and the aldehydic nucleus by distilling the substance with dilute sulphuric acid and manganese dioxide and testing the filtrate with magenta-sulphurous acid reagent. With bromine, novocaine yields a yellow precipitate, which dissolves when the mixture is heated.   W. P. S.

The Colorimetric Estimation of Hæmoglobin as Acid Hæmatin. LADISLAUS BERCZELLER (*Biochem. Zeitsch.*, 1918, **87**, 23—35).—By means of an Autenrieth colorimeter, hæmoglobin can be estimated as acid hæmatin, when a washed suspension of corpuscles is employed. The method cannot, however, be employed for determining the amount of hæmolysis in, for example, the Wassermann reaction, as it is interfered with both by the presence of serum and the solution of the antigen in organic solvents.
                                                            S. B. S.

Tryptoproteases. M. FRANCESCO (*Arch. farm. sper. sci. aff.*, 1917, **24**, 3—22; from *Physiol. Abstr.*, 1918, **3**, 165).—From a comparative study of nine methods for determining the presence of trypsin, the author recommends the gelatin method of Fermi as the most delicate and trustworthy. It is fifty times as sensitive as the serum and casein methods for the protease of some of the pathogenic bacteria.   S. B. S.

General and Physical Chemistry.

Comparative Study of the Flame and Furnace Spectra of Iron. G. A. Hemsalech (*Phil. Mag.*, 1918, [vi], **36**, 209—230).—A direct comparison has been made of the flame and furnace spectra of iron by the use of the same dispersion apparatus in the two series of observations. In the production of the furnace spectrum, finely divided oxide of iron was introduced into an electrically heated carbon tube by means of a current of air which had previously passed through a glass bulb enclosing an arc burning between iron electrodes.

The furnace spectrum makes its appearance at about 1500°, and at this temperature the spectrum is the same as that obtained with an air flame burning in coal gas. Up to about 2400°, the flame spectra are identical with those given by the furnace at corresponding temperatures. This identity suggests that the cause of the emission is the same under the different conditions obtaining in the two series of observations, and the author supposes that the spectrum is directly due to the thermochemical dissociation of iron compounds. Above 2500°, the furnace spectrum undergoes a radical change, and it is supposed that this is due to the electrical conduction of the vapour.

In contrast with the above parallelism between flame and furnace spectra, it is noteworthy that the iron spectrum emitted by iron in the inner cone of an air–coal gas flame, the temperature of which is less than 1700°, contains lines which are entirely absent from the flame or furnace spectrum up to 2500°. Some of these lines are shown very feebly by an oxy-acetylene flame at a temperature of about 2700°, but their intensity is very much less than that of the lines in the explosive region of the air–coal gas flame. This anomaly in the behaviour of the low temperature Bunsen cone is attributed to the affinity of iron for nitrogen, with the formation of a nitride. The cause of the emission is accordingly chemical, and the chemical excitation at a comparatively low temperature is equivalent to that produced by thermochemical excitation at a very much higher temperature. In its development, the cone emission approaches, in fact, that of the self-induction spark.

<div align="right">H. M. D.</div>

Spectrochemical Notes. I. Polyketo-compounds. II. Allene and Keten. III. Spectrochemical Practice. K. von Auwers (*Ber.*, 1918, **51**, 1116—1133).—I. This section discusses the influence of the introduction of conjugated carbonyl groups in a compound on the refraction and dispersion. As the subjoined table shows, the simple conjugation –CO·CO– causes unimportant exaltations, which are not much more marked when further

carbonyl groups are introduced, but conjugations with an ethylene linking of the types $-C{:}C{\cdot}C{:}O$, and especially $-C{:}C{-}CO{\cdot}CO{-}$, cause very considerable exaltations in refraction and dispersion.

Formula.	$E\Sigma_a$.	$E\Sigma_D$.	$E\Sigma_\beta - \Sigma_a$.	$E\Sigma_\gamma - \Sigma_a$.
$CH_3{\cdot}CO{\cdot}COMe$	$+0{\cdot}42$	$+0{\cdot}41$	$+9\%$	—
$CO_2Et{\cdot}CO_2Et$	$0{\cdot}27$	$0{\cdot}27$	4%	4%
$CH_3{\cdot}CO{\cdot}CO{\cdot}CO_2Et$	$0{\cdot}60$	$0{\cdot}60$	—	—
$CO(CO_2Et)_2$	$0{\cdot}57$	$0{\cdot}56$	10%	—
$C_2O_2(CO_2Et)_2$	$0{\cdot}68$	$0{\cdot}68$	—	—
$C_6H_5{\cdot}CO{\cdot}COMe$....................	$1{\cdot}01$	$1{\cdot}05$	—	—
$COPh{\cdot}CO{\cdot}COMe$	$1{\cdot}37$	$1{\cdot}45$	—	—
$(p)OMe{\cdot}C_6H$ $Me{\cdot}CO{\cdot}COMe$ ...	$1{\cdot}27$	$1{\cdot}35$	80%	—
$(p)OEt{\cdot}C_6H_3Me{\cdot}CO{\cdot}COMe$	$1{\cdot}46$	$1{\cdot}53$	78%	—
$C_6H_5{\cdot}CO{\cdot}CO_2Et$	$0{\cdot}89$	$0{\cdot}94$	46%	52%

Most of the above compounds are already well known, but complete physical data are recorded in each case, for which the original should be consulted. p-*Ethoxy-o-tolyl methyl diketone*,

$$OEt{\cdot}C_6H_3Me{\cdot}CO{\cdot}COMe,$$
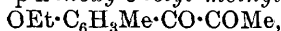
appears to be new. It crystallises in glassy prisms, m. p. 63—64°, has D_4^{65} $1{\cdot}0524$, n_a $1{\cdot}50733$, n_D $1{\cdot}51270$, n_β $1{\cdot}52888$, at 65°, and is prepared as follows. o-Propionyl-p-cresol is ethylated by means of ethyl sulphate, the p-*ethoxy-o-tolyl ethyl ketone*, m. p. 50—51°, is treated with amyl nitrite and hydrochloric acid, and the *oxime*, m. p. 105—106°, is hydrolysed by boiling sulphuric acid.

II. In this chapter, it is shown that compounds with cumulated ethylene linkings exhibit considerable exaltations in refraction and dispersion. For example, $\alpha\alpha$-dimethylallene, $CMe_2{:}C{:}CH_2$, b. p. 39—40·5°, has $E\Sigma_a$ $+0{\cdot}60$, $E\Sigma_D$ $0{\cdot}59$, $E\Sigma_\beta - \Sigma_a + 21\%$, $E\Sigma_\gamma - \Sigma_a$ 18%. This is contrary to Brühl's rule (*Ber.*, 1907, **40**, 1160), but is supported by the results obtained by Mereschkowski with s-tetramethylallene and $\alpha\alpha$-diethylallene (A., 1914, i, 369). The influence of adjacent pairs of ethylene linkings is by no means so great as that of conjugated double bonds, however; piperylene,

$$CHMe{:}CH{\cdot}CH{:}CH_2,$$
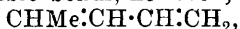
for example, has $E\Sigma_a + 1{\cdot}81$, $E\Sigma_D$ $2{\cdot}10$, $E\Sigma_\gamma - \Sigma_a + 53\%$.

Ketens have a similar system of cumulated double bonds, $-C{:}C{:}O$, but this system has no special optical influence, as the following table shows:

Formula.	$E\Sigma_a^{i'}$.	$E\Sigma_D$.	$E\Sigma_\beta - \Sigma_a$.
$Ph_2C{:}O$	$+0{\cdot}91$	$+1{\cdot}00$	—
$Ph_2C{:}CH_2$	$0{\cdot}88$	$0{\cdot}95$	—
$Ph_2C{:}C{:}O$	$0{\cdot}86$	$0{\cdot}92$	—
$Et_2C{:}C{:}O$	$-0{\cdot}08$	$-0{\cdot}09$	-2%

The polymeride of diethylketen, namely, $1{:}1{:}3{:}3$-tetraethyl*cyclo*butan-2:4-dione, has $E\Sigma_a + 0{\cdot}27$, $E\Sigma_D + 0{\cdot}25$, $E\Sigma_\beta - \Sigma_a + 4\%$, $E\Sigma_\gamma - \Sigma_a + 1\%$, the increments being of the order normally associated with the four-membered ring system.

III. For the determination of the density of molten substances, the author recommends an ordinary pyknometer with a portion of

one of its capillaries, about 2 cm. long, graduated in millimetres. Such an instrument is calibrated for different points along this scale, and in an actual determination the position of the liquid in the tube is noted. J. C. W.

Effects of Ring Closure on Spectrochemical Properties. I. Saturated Iso- and Hetero-cyclic Compounds, Unsaturated Isocyclic Substances, and the Question of the Constitution of Benzene. K. VON AUWERS (*Annalen*, 1918, **415**, 98—168).—The author surveys a large field of material, and arrives at the following generalisations. Compounds the molecules of which contain one or more rings (isocyclic or heterocyclic) without linkings of any kind are optically normal; only when the ring is under tension do the molecular refraction and dispersion exhibit exaltation or depression. The spectrochemical character is unchanged when a saturated side-chain closes to form a ring; for example, the pairs *o*-tolyl methyl ether and coumaran and *o*-tolyl ethyl ether and chroman are optically identical, and the same holds for a large number of other coumarans and phenolic ethers. The closure of an unsaturated side-chain to a ring causes a weakening of the optical properties, which is the more pronounced the more unsaturated is the chain; for example, styrene derivatives and indene derivatives, acyclic dienes and cyclic dienes, and acyclic trienes and cyclic trienes. Alkyl groups and other substituents produce an effect opposed to that of ring closure in unsaturated compounds. Exceptions occur to all these generalisations.

Contrary to earlier views, double linkings in open and in closed chains are not optically equivalent, the spectrochemical effect of cyclic double linkings being quite generally slighter than that of ethylenic linkings.

The two physico-chemical methods of investigation, spectrochemistry and thermochemistry, both decide against the view that benzene and its hydrogenated derivatives are different in their innermost structure, and all the physical and chemical facts ally themselves best to a benzene formula containing three double linkings.

The densities and refractive indices of a number of compounds have been redetermined, and new determinations have been made in the case of a large number of coumarans, chromans, phenolic ethers, ketones, and indene derivatives.

The following substances are new: as.-m-*xylyl ethyl ether*, b. p. 202—203°, $D_4^{13\cdot95}$ 0·9487, n_σ 1·50297, n_D 1·50692, n_β 1·51874, n_γ 1·52872 at 13·95°; 5-*bromo-o-tolyl ethyl ether*, b. p. 238—240°, $D_4^{11\cdot35}$ 1·3592, n_α 1·54387, n_D 1·54858, n_β 1·56186, n_γ 1·57332; 6-*ethoxy*-m-*toluic acid*, needles, m. p. 200—201°, and its *ethyl* ester, b. p. 274—275°, $D_4^{15\cdot1}$ 1·0618, n_α 1·51443, n_D 1·51908, n_β 1·53259, n_γ 1·54428 at 15·1°; and 1-*methyl*-ac-*tetrahydro-a-naphthol*, colourless leaflets, m. p. 88—89°. C. S.

17—2

Quinone-imide Dyes. X. Absorption Spectra of the Simplest Triphenylmethane Dyes. F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 915—922. Compare this vol., i, 311).— Tables are given which record the shades of colour and absorption spectra of the various series of salts of triphenylcarbinol, its mono-, di-, and tri-amino-, and mono-, di-, and tri-dimethylamino-derivatives, the substituents being in the para-positions. It is shown that the highest salts in all cases, ranging from the di-acid salt of triphenylcarbinol to the tetra-acid salts of magenta and crystal-violet, and obtained by dissolving the dyes in concentrated sulphuric acid, give pure yellow solutions with practically the same absorption band, beginning at about λ 480—490 $\mu\mu$.   J. C. W.

Quinone-imide Dyes. XI. Absorption Spectra of some Amino-derivatives of Naphthaphenazoxonium. F. KEHRMANN and M. SANDOZ (*Ber.*, 1918, **51**, 923—928).—The absorption spectra of some amino-derivatives of 7 : 12-naphthaphenoxazine and their salts are recorded by tables of curves. The 5-amine is lemon-yellow and gives orange-yellow mono-acid salts and dark blood-red di-acid salts, all having the para-quinonoid configuration. The 9-amine is orange-yellow and gives magenta-coloured mono-acid, greenish-blue di-acid, and bluish-violet tri-acid salts. The 5 : 9-diamine is orange-coloured, and its salts are as follow: mono-, violet-blue with red fluorescence; di-, orange-yellow; tri-, dark blood-red. The 9-di-methylamino-derivative forms violet mono-acid and green di-acid salts.   J. C. W.

Action of Light on Crystals. FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1918, **24**, 222—237).—The extinction of crystals and the phototropic changes occasioned by light of short wave-length have been examined in the case of β-tetrachloro-α-ketonaphthalene. It is shown that no changes, other than the characteristic colour changes, are brought about in the crystallographic properties of β-tetrachloro-α-ketonaphthalene by the action of light of short wave-length. The axial ratio remains constant even under strong illumination. The absorption spectrum of the crystals varies very much with the electric vector of the entering plane polarised light. When the crystal is not excited, two absorption bands, 395 $\mu\mu$ and 375 $\mu\mu$, are observed if the entering ray is vibrating in the direction of the *c*-axis, but if the entering ray is vibrating in the *a*-*b*-plane, an end absorption at 420 $\mu\mu$ is observed. With excited crystals and the entering light in the *c*-direction, there is no change in the absorption spectrum, whilst in the *a*-*b*-plane the absorption is much greater, and an absorption band appears in the yellow-green; this is due to the phototropic colouring. The absorption spectrum of the solutions of β-tetrachloro-α-ketonaphthalene in ether and benzene shows no characteristic bands, but in the long wave-length ultra-violet two obvious steps appear in the same positions as the bands observed with the crystals. Hence it appears that the solid and dissolved molecules are identical. The effect for an equal

quantity of energy when the electric vector is in the c-direction is greater than when it is in the a-b-plane, since the absorption is greater in the first case than in the second. The lighting up of the crystal by plane polarised yellow light only occurs when the electric vector vibrates in the a-b-plane. The maximum excitation of β-tetrachloro-α-ketonaphthalene will therefore only occur when plane polarised light swinging in the c-direction is allowed to fall on it, since in this case the light produces no brightening in the opposite direction. The fact that the coloration does not occur in the solution, but only in the crystal, shows that the ordered, closely packed orientation of the molecules in the crystal is the cause of the effect. The two possible formulæ for β-tetrachloro-α-ketonaphthalene are considered in the light of the present results, and it is shown that one only is in accord with them, namely, that with Cl_2 in the α-position. J. F. S.

Temperature-coefficients of the Action of Light on the Chlorine–Hydrogen Mixture with Monochromatic Light. M. PADOA and C. BUTIRONI (*Gazzetta*, 1917, **47**, ii, 6—9).—The velocities of the combination of hydrogen and chlorine at 10°, 20°, 30°, and 40°, and for lights of different wave-lengths, have been measured, the mean temperature-coefficients being as follows : white light, 1·29 ; green ($\lambda = 550$—530), 1·50 ; blue ($\lambda = 490$—470), 1·31 ; violet ($\lambda = 460$ —440), 1·21 ; ultra-violet ($\lambda = 400$—350), 1·17.
T. H. P.

History of Substances Sensitive to Light. BORUTTAU (*Zeitsch. angew. Chem.*, 1918, **31**, 139—140).—The discovery of the colour change of silver salts under the influence of light is stated to be mentioned first by Konrad Gessner in 1565 in his work, " De omni verum fossilium genere libri aliquot," and not by Fabricius, as erroneously supposed. Gessner describes the darkening of natural hornsilver when exposed to light. The later history of the subject is traversed. H. J. H.

The Parent-substance of Actinium; a New Radioactive Element of long Life-period. OTTO HAHN and 'LISE MEITNER (*Physikal. Zeitsch.*, 1918, **19**, 208—218. Compare Soddy, Cranston, and Hitchins, this vol., ii, 211).—The history of the long search for the parent of actinium is detailed. The value for the half-period of actinium itself, given provisionally by Mme. Curie as of the order of thirty years, has been confirmed for an actinium preparation studied during seven years, as well as for several more recently prepared specimens. Early attempts to detect the parent of actinium in uranium salts led to no result. In the first successful experiment, 21 grams of powdered pitchblende were treated with hot concentrated nitric acid. Part of the undissolved siliceous residue, mixed with some mg. of potassium tantalum fluoride, was treated with hydrofluoric acid, which dissolved it for the most part, and the solution, after filtration and evaporation, was

evaporated with concentrated sulphuric acid. Concentrated nitric acid dissolved most of the residue. The undissolved part was mounted on an aluminium sheet (Prep. I), and was found to give α-rays, which remained constant for some weeks and then slowly increased when the preparation was tested bare. Tested so as to cut out the α-rays of low range, the growth of the radiation was much more marked, increasing some sixfold in the course of a year, the growth being linear with the time after the first few weeks. This indicated that the siliceous residues from pitchblende contained the sought-for parent of the actinium, resembling tantalum in chemical character and giving α-rays of low range in producing actinium, the products of which give α-rays of long range.

This view was completely confirmed by working with larger quantities of rich pitchblende residues obtained from the Chinin-fabrik, Brunswick. These residues, after a preliminary treatment with hydrochloric acid in presence of a few mg. of tantalic acid, and after the addition of a few mg. of thorium nitrate, were treated as detailed for Prep. I. The rapid growth of the more penetrating α-radiation was confirmed, and the growth of an active deposit also found. After three weeks, no active deposit could be detected, but after five months an easily measurable quantity was found, and its growth thereafter could be followed and the active deposit itself shown to be that of actinium. The growth of the actinium emana-tion with time was also observed. For the measurement of the range of the α-rays and the quantitative study of the growth of emanation and active deposit, preparations were worked up by Giesel at the Chininfabrik from 1 kilogram of pitchblende residues by the method described. The weight was reduced to 16 grams, and from this 73 mg., mainly tantalic acid, was obtained as a white powder, one thousand times as active as the material from which it was separated, and weight for weight forty-six times as active as uranium oxide. Assuming that 8% of the uranium atoms disintegrating produce "protoactinium," the quantity in the 73 mg. is that in equilibrium with 86 grams of uranium.

Concordant measurements of the range of the α-rays gave 3·314 cm. in air at 0° and 760 mm. (wrongly given in the summary and elsewhere as 3·14 cm.). From the Geiger Nuttall relation, using the values for the constants A and B deduced from observa-tions of the range of the α-rays of radio-actinium, the calculated half-life period is 180,000 years, but using the values found for the α-rays of actinium-X, the half-period calculated is 1200 years. It is of interest that in the latter research, Meyer, Hess, and Paneth observed for actinium itself a very feeble α-radiation of range 3·38 cm., which was probably due to admixed proto-actinium.

Using 45 mg. of the preparation, the growth of the actinium emanation was followed for 100 days, in which time the amount increased to thirty times that present at the first measurement four days from preparation. After the initial period of gradually increasing rate of growth, extending over forty days, due to the successive generation of radio-actinium and actinium-X, the growth

continued linearly with the time. The growth of the active deposit from 9·5 mg. of the preparation was also followed. The active deposit showed a sevenfold increase between the first and the third month.

Protoactinium is one of the five new radio-elements occupying a place in the periodic table hitherto vacant, and the determination of its spectrum and atomic weight should be practicable. For each 1 gram of radium in uranium minerals there should be 60 mg. of protoactinium if its life is 1200 years and 9 grams if its life is 180,000 years. Its atomic weight is either 230 or 234, according as the actinium series is derived from uranium-*II* or uranium-*I*, and the former is indicated according to the Fajans generalisation, between atomic weight and life-period of isotopes, which makes the most probable value for the atomic weight of radioactinium 226. Its separation in quantity from pitchblende residue should enable purer preparations of actinium to be prepared than have yet been got, analogously to the preparation of radiothorium from old mesothorium preparations. It should prove to be a radioactive substance, the α-activity of which increases sixfold during the lapse of some generations and then remains constant and permanent.

F. S.

The Life-period of Radiothorium, Mesothorium, and Thorium. 'LISE MEITNER (*Physikal. Zeitsch.*, 1918, **19**, 257—263).

—Measurements extended over seven years of α-, β-, and also γ-rays of six preparations of radiothorium prepared by electrolytic and chemical methods all gave quite linear logarithmic decay curves, the half-period for the six preparations varying between 690 and 698 days, the mean being 696 days = 1·905 years, accurate to about 1%.

The life-period of mesothorium-*I* was determined by a new method from the growth of radiothorium from mesothorium initially quite free from radiothorium. Mesothorium as free as possible from radium was prepared from mantle-ash by the firm of Knöfler and Co., Plötzensee, the preparation being crystallised three times at fortnightly intervals to remove radiothorium and its products. Tested for radium, it was found that only 0·8% of the β-rays and 0·62% of the γ-rays were due to this element, which was corrected for. By comparing the curve obtained with theoretical curves drawn for various periods of mesothorium, the results were found to agree well with a value 6·7 years for the half-period. This new value was checked by observation of the decay of the activity of a preparation of mesothorium, prepared by Hahn in 1906 and 7·1 years old at the commencement of the measurements. The period again found, 6·7 years, is considerably higher than the value, 5·5 years, for the half-period of mesothorium commonly accepted. The maximum of the α-activity of a mesothorium preparation is calculated to be 4·83 years from preparation, and of the γ-rays, through 0·5 cm. of lead, 3·34 years. For preparations of equal α-activity of radium and radiothorium respectively in equilibrium with their

a-ray products, the γ-rays of radium are 1·5 times those of radiothorium and 0·9 times those of radiothorium and mesothorium in equilibrium.

The life-period of thorium was calculated by a somewhat elaborate method depending on a comparison of the a-rays of radium and thorium preparations under defined conditions, and found to be $2\cdot37 \times 10^{10}$ years (period of half-change), which is somewhat greater than previous estimates—1·28 (Geiger and Rutherford), 1·86 (McCoy), 1·5($\times 10^{10}$ years) (Heiman). The above value is reduced to $2\cdot16 \times 10^{10}$ years if the just published value for the half-period of radium is taken as 1580 years (Hess and Lawson).   F. S.

Radioactivity in Natural Sardinian Materials, with Minerogenetic Particulars. AURELIO SERRA (*Gazzetta*, 1917, **47**, ii, 1—5).—A Sardinian porphyritic granite is found to be radioactive, its activity being $a = 0\cdot00010$. The activity is shown to be due to the presence in the rock of uraniferous biotite; the biotite has been subjected to the action of water which has previously traversed strata of uraniferous mica, the thickness of the latter determining the greater or less radioactive power.   T. H. P.

Abnormality of Strong Electrolytes. II. Electrical Conductivity of Non-aqueous Solutions. JNANENDRA CHANDRA GHOSH (T., 1918, **113**, 627—638).—In a previous paper (compare this vol., ii, 215) it has been shown that the variation of the conductivity of aqueous solutions of salts with dilution can be satisfactorily accounted for by equations which the author has derived from certain assumptions relative to the nature of electrolytes. It is now shown that these equations may be applied with equal success to the conductivity of non-aqueous solutions of strong electrolytes. In all, some thirty different solvents have been examined with reference to the influence of dilution on the conductivity of one or more dissolved electrolytes.

The behaviour of Walden's "normal electrolyte" (tetraethylammonium iodide) can only be explained on the assumption that it at first undergoes polymerisation and then ionises as a ternary electrolyte in accordance with the equation $(NEt_4I)_2 = 2NEt_4^{\boldsymbol{\cdot}} + I_2''$ or $(NEt_4I)_2 = (NEt_4)_2^{\boldsymbol{\cdot\cdot}} + 2I'$.

From his observations on the conductivity of tetraethylammonium iodide in different solvents, Walden found that the product of the dielectric constant (D) and the cube root of the dilution (V), for which the degree of ionisation has a common value, is the same for all solvents. In other words, $D \sqrt[3]{V}$ is independent of the nature of the solvent. It is shown that this empirical relation follows at once from the author's equations, in which μ_r/μ_∞ represents, however, the activity coefficient and not the degree of ionisation in the Arrhenius sense.   H. M. D.

Electromotive Behaviour of Oxygen and its Anodic Evolution below the Reversible Oxygen Potential. G. GRUBE and B. DULK (*Zeitsch. Elektrochem.*, 1918, **24**, 237—248).—With

the object of ascertaining the nature of the process occurring on an anodically polarised platinum electrode during the evolution of oxygen, the authors have measured the oxygen potential on such an electrode which at the same time is polarised by a measured direct current and an alternating current. The latter acts in the same way as a depolariser of measured strength. Series of measurements are recorded for alternating currents up to 4·0 amperes and current densities up to 0·287 ampere per sq. cm. All measurements were made at 20° and in 2N-sulphuric acid. A further series of measurements is recorded for N-sodium hydroxide for depolarising currents up to 5·0 amperes and 0·358 ampere per sq cm. current density. It is shown that the depolarising action of the alternating current is due to the reduction of a platinum oxide by the cathodic component. If the alternating current is slowly increased in strength along with a steady direct current, the oxygen potential (that is, the anode potential) falls below the value for the reversible formation of oxygen. The potential curve obtained from the measurements falls into three parts which are separated by inflection points. The highest of these curves corresponds with $\epsilon_h = 2·0 - 1·5$ volts, the next to $\epsilon_h = 1·5 - 1·23$ volts, and the lowest with $\epsilon_h = 1·23 - 1·0$ volts. This compels the assumption that the electromotive activity of oxygen above its equilibrium potential causes the formation of two different platinum oxides. The oxide which is active over the region $\epsilon_h = 2·0 - 1·5$ volts is unknown and is higher than PtO_3. In the region $\epsilon_h = 1·5 - 1·23$ volts, the dissolved oxide PtO_3 brings about the evolution of oxygen, whilst below 1·23 volts the evolution of oxygen is due to the reaction $H_2O_2 + O \longrightarrow H_2O + O_2$. The hydrogen peroxide necessary for this change is produced by alternating current on the anode. The most probable value for the oxygen potential is given as $\epsilon_h = +1·23$ volts.

J. F. S.

Kinetics of Reactions with Electrolytes in Homogeneous Systems. RUD. WEGSCHEIDER (*Monatsh.*, 1918, **39**, 15—86).—A theoretical paper in which the kinetics of the various types of reactions with electrolytes are discussed. Replaceable electrolytes are characterised as those which have the same type of formulæ, are not ionised in stages, have the same dissociation constant, have either a common ion and only one unlike ion, or are binary electrolytes. In the case where all the electrolytes are replaceable, it is shown that they have the same degree of dissociation, and this depends on the total concentration of the electrolytes only. With electrolytes having dissimilar ions, the degree of dissociation does not depend on the electrolyte, but on the nature of the ion-forming radicles. If in a reaction only non-electrolytes and replaceable electrolytes are present, then the degree of dissociation does not change if the total concentration of the electrolytes does not change. In general, the course of an electrolytic reaction is different in accordance with whether a separation of electrolyte occurs or not. A statement is evolved which represents the change in dissociation of a non-replaceable electrolyte, in the presence of

17*

replaceable electrolytes, during the course of a reaction with constant total ion concentration. The relationship between the velocity constant, as obtained from the law of mass action, and the course of the reaction is examined for the case where only one electrolyte is active (1) as relating to the undissociated molecule, and (2) either as relating to all the ions or only to one ion of a given molecule. The case of simultaneous reactions with a single electrolyte, and reactions with two electrolytes are also considered. The regularities found in these cases are illustrated by means of well-investigated reactions. In the case of the barium catalysis of Abel and the cation catalysis of Holmberg, it is shown that the formulæ obtained are quantitatively accurate, despite the presence of strong electrolytes. It is clearly shown that the electrolytic dissociation theory is not only not disproved by chemical kinetics, but is strongly supported. Further, the view of the overwhelming importance of the ionic condition in bringing about chemical reactions must be very much restricted. It is also shown on what conditions the divergencies from the laws of chemical kinetics depend, and also how the sensitiveness of kinetic calculations depends on uncertainty of the value of the degree of dissociation.   J. F. S.

Electrochemical Behaviour of Molybdenum and some Molybdenum Compounds. KUNO WOLF (*Diss. Tech. Hochschule Aachen*, 1918, 38 pp.; from *Chem. Zentr.*, 1918, i, 608—609).— For the electrolytic estimation of molybdenum, the metal is separated in the form of the hydrated sesquioxide, and is then dried and converted into the trioxide by ignition at 425°; sublimation occurs at 450°. The separated sesquioxide or hydroxide has an electrolytic and at first a pseudo-metallic conductivity. On account of the poor yield, the electrolytic preparation of hydrated molybdenum sesquioxide is not practicable. Pure molybdenum, freezing point 2250°, D 8·95, prepared from the commercial metal, can be formed into sticks without pressure, treatment with a current of hydrogen for five to six hours at 2250°, however being necessary for the reduction of included oxides. Pure molybdenum free from oxide is converted by chlorine into black, deliquescent molybdenum pentachloride, which on treatment with hydrogen at 250° yields the deep brownish-red, amorphous trichloride; this, when heated in a current of carbon dioxide, decomposes gradually with formation of the volatile tetrachloride and the refractory pale yellow, amorphous dichloride; the lower chlorides of molybdenum are much more stable than the higher towards air and water. In the preparation of the dichloride from molybdenum, it is important to exclude every trace of oxygen, because when heated in air the dichloride gives a cloudy white sublimate and a black residue of oxide. The dichloride gives yellow solutions in aqueous sodium hydroxide or potassium hydroxide, which deposit the black dihydroxide when boiled. The alcoholic solution conducts the electric current, the molecular conductivity increasing on dilution; hydrogen and

the oxychloride, $Mo_3(OH)_2Cl_4$, and sometimes molybdenum, are liberated at the cathode, whilst acetaldehyde and ethyl chloride are formed at the anode. By combination with an alcoholic calomel electrode, the electrolytic potential for molybdenum/molybdenum dichloride dissolved in alcohol has a value 0·552 volt referred to the hydrogen electrode as zero. In the potential series molybdenum falls between mercurous mercury and tervalent antimony. The alteration of the potential with dilution corresponds only qualitatively with Nernst's formula. D. F. T.

Electric Nebulæ of Antipyretica. H. ZWAARDEMAKER and H. ZEEHUISEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 1272—1277).—The electric charge which is developed when a solution of an odorous substance in water is sprayed (Zwaardemaker, A., 1917, ii, 63; see also Backman, A., 1917, i, 498) is also produced by solutions of other substances, odorous or odourless, such as saponins, glucosides, alkaloids, antipyretica, and other physiologically active substances. In order to produce the electric phenomenon, the substance, added to water and sprayed with it, must satisfy certain conditions: (1) it must be soluble in water; (2) it must lower the surface tension; (3) it must volatilise when spread over a large evaporation area. Inorganic acids and salts, glycerol, sugars, dextrin, lecithin, and albumin do not produce the phenomenon.

A saturated aqueous solution of the antipyretic alkaloids, quinine, quinidine, cinchonine, cinchonidine, etc., sprayed under an over-pressure of 2 atmos., charges positively a screen at a distance of about 25 cm., the air around it and at some distance from it being charged negatively. The effect is less pronounced than that caused by odorous substances.

The charge produced by salicylic acid and its derivatives varies from zero in the case of insoluble phenyl and benzyl salicylates to a moderate effect with salts of salicylic acid and to effects caused by salicylic acid and its liquid derivatives, which are sometimes stronger than those due to typical odorous substances such as camphor. The salts owe their electrifying power to the anion; the cation lessens the charge of the nebula. The optimal electrifying power of salicylic acid is produced by a millinormal solution.

The third group of antipyretica examined comprises quinoline derivatives, pyrazoles, and *p*-aminophenols. The electric phenomenon is produced by pyramidone, phenacetin, and citrophen with moderate intensity, somewhat more strongly by kairine, and is extremely distinct in the case of antipyrine, salipyrine, acetopyrine, tussol, antifebrin, and euphorine.

To obtain normal results, the sprayer must be earthed. The magnitude of the electric charge is greatly affected by the addition of sucrose or sodium chloride to the solution. The charge is always increased by the former, but the effect of sodium chloride depends on its concentration. C. S.

New Cryoscopic Tube and Method. GIUSEPPE ODDO (*Gazzetta*, 1917, **47**, ii, 188—199).—The tube described and figured differs from the usual form in having a wide side-tube set obliquely to the main tube near the bottom of the latter. This tube is closed with a stopper, and is used for the rapid introduction of solvent and substance. The arrangement is intended more especially for working with very hygroscopic substances.   R. V. S.

Condition of Substances in Solution in Absolute Sulphuric Acid. VI. G. ODDO and A. CASALINO (*Gazzetta*, 1917, **47**, ii, 200—232. Compare Oddo and Scandola, A., 1910, ii, 1035).—Continuing this investigation, the authors have studied the behaviour of thirty-one organic acids dissolved in absolute sulphuric acid. In the case of the monocarboxylic acids, such as *n*-butyric acid, the molecular weight observed is a little more than 50% of the true molecular weight, indicating that these acids form dissociated oxonium salts. Among the dicarboxylic acids, oxalic acid gives the highest values, exceeding 80% of the molecular weight, and the percentages observed increase with the concentration. The rest of the acids examined in this series have apparent molecular weights which are smaller the more distant the two carboxyls, and the figures obtained decrease with the concentration. The conclusions which may be drawn from the experimental data as to the constitution of solvent and solutes are discussed.   R. V. S.

Condition of Substances in Solution in Absolute Sulphuric Acid. VII. G. ODDO and A. CASALINO (*Gazzetta*, 1917, **47**, ii, 232—243. Compare preceding abstract).—This paper deals with the behaviour of certain aldehydes, ketones, lactones, and anhydrides in absolute sulphuric acid. The aldehydes, ketones, and lactones behave like the monobasic acids described in the preceding paper. Acetic anhydride has 48·9—34·3% of its true molecular weight, succinic anhydride 89·1—68·4%, and phthalic anhydride 111·7—89·0%. The variations in each case correspond with varying concentrations.   R. V. S.

The Laws of the Vapour Pressures of Water and of other Vapours. PIETRO ENRICO BRUNELLI (*Nuovo Cim.*, 1917, [vi], **14**, ii, 55—68).—The formula $\log p = 23\cdot08647 - 4\cdot5 \log T - 2980\cdot46/T - 0\cdot00278T + 0\cdot000002825T^2$, where p is the pressure in mm. of mercury and T is taken to be $273\cdot09 + t$, gives the vapour pressure of water more exactly and over a longer range of temperature than any of those hitherto proposed. Similar formulæ are given for carbon dioxide and ammonia, and in these cases also the agreement with observed values is satisfactory.   R. V. S.

The Saturated Vapour Pressures of Substances of High Atomicity. E. ARIÈS (*Compt. rend.*, 1918, **167**, 267—270. Compare this vol., ii, 294).—The formula given for compounds containing more than eight atoms in their molecule is $\Pi = \tau^8 Z/x$, where

$x = \tau^2 \Gamma$, and formulæ are given in the cases of pentane, hexane, heptane, and octane showing the variations of Γ with the reduced temperature τ. The calculated values are in fairly close agreement with those observed by Young for these four hydrocarbons.

W. G.

The Manipulation of Volatile Substances. III. ALFRED STOCK (*Ber.*, 1918, **51**, 983—989. Compare A., 1917, ii, 442).— The following pieces of apparatus are described with diagrams, and an account is given of their applications.

I. An improved form of gas-holder for substances which can be condensed by liquid air (*ibid.*).

II. (*a*) An arrangement for filling a tube with a gas or mixture, without exposure to the air, and sealing it, for example, a mixture of hydrogen bromide, monosilane, SiH_4, and aluminium bromide, and (*b*) a simple device, "vacuum tube opener," for breaking the capillary of a sealed tube and leading off the gases it may contain without exposure to the air.

III. A simple apparatus for analysing a gaseous mixture by measuring the pressure of the gas left uncondensed at different temperatures, suitable for cases in which the uncondensable impurity is not more than 25%, and is, of course, insoluble in the liquefied gas. The construction of the apparatus is sufficiently clear from the annexed diagram, and it is used as follows. A suitable volume of the gas is admitted into the measuring tube over mercury, which is easily done without disturbing the column in the side-limb, this serving as a manometer. The open end is closed with a good stopper, and the constricted end is then immersed in the cooling bath, such as liquid air, and when the levels of the mercury columns are steady, the volume of the unabsorbed gas is read off and the pressure upon it found from the difference in the mercury levels. The temperature of the residual gas will not be uniformly the same as the initial gas, for part of it will be within the range of the cooling-bath. A sufficiently accurate correction may be made by noting the contraction in volume when the tube is filled with air and the constricted end is placed in the bath, the immersion being to the same depth as in an actual analysis. Having now corrected the initial and final volumes to *N.T.P.*, the determination of the proportion of unabsorbed gas is simple.
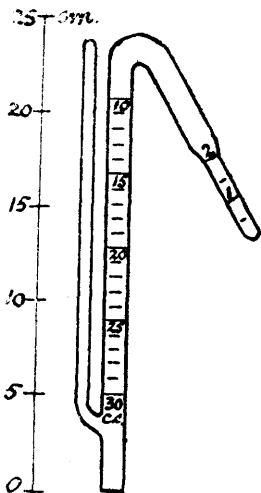
J. C. W.

Thermochemical Studies. DANIEL LAGERLÖF (*J. pr. Chem.*, 1918, [ii], **97**, 137—140).—As an extension of the earlier paper

(this vol., ii, 62), it is shown that if Zubow's experimental values are corrected by a divisor 1·00888 instead of 1·007, as suggested by Roth, the results thus obtained for *n*-hexane and *n*-octane are almost identical with those calculated by the author.   D. F. T.

The Characteristic Equation of Fluids. PIERRE WEISS (*Compt. rend.*, 1918, **167**, 293—296. Compare this vol., ii, 291).— A mathematical discussion of the subject.   W. G.

The Characteristic Equation of Fluids. PIERRE WEISS (*Compt. rend.*, 1918, **167**, 364—366. Compare preceding abstract). —By combining the equation expressing the law of dilatation (*loc. cit.*) and the general equation $\Pi = a/v^\eta$ for the law of internal pressure, the characteristic equation of fluids becomes

$$(p + a/v^\eta)(v - b) = \zeta RT,$$

where a, b, ζ, and η are constants, and R is the constant of perfect gases. Very different combinations of these constants may occur for the same substance, but generally the values $\zeta = 1$ and $\eta = 2$ in the region of large volumes, and in that of high densities ζ is great and the co-volume is small.   W. G.

The Molecular Condition of Alloys in the Crystalline State and its Relation with the Form of the Equilibrium Diagram. G. MASING (*Int. Zeitsch. Metallo.*, 1916, **9**, 21—37; from *Chem. Zentr.*, 1918, i, 703—704).—The idea of extensive dissociation in compounds which over a considerable range of concentration are able to form mixed crystals with the two components is not opposed to crystallographic or general considerations; indeed, from the point of view of the phase rule also, dissociation is possible in the solid state with such compounds as opposed to compounds which are unable to form mixed crystals. A compound which is largely dissociated in the solid state and is capable of taking only small quantities of the components into solid solution can, as an independent crystalline entity, possess a slight solvent power for the components only over a small temperature interval in the immediate neighbourhood of the temperature boundary of its area of existence, for example, of the m. p. A highly dissociated compound which forms mixed crystals with its components over a wide range of temperature must also give rise to homogeneous mixed crystals over a large interval of concentration. If, however, the crystalline form of a compound possessing very limited miscibility is stable in the solid state over a wide range of temperature, the compound can be only slightly dissociated, and the extent of the possible dissociation is proportional to the breadth of the area of existence of the homogeneous crystals. It is thus possible from the equilibrium diagram to draw a conclusion as to the molecular condition of an alloy, but the decision concerns only the upper limit of the degree of dissociation; an extensive range of solubility in the solid state is not trustworthy evidence of extensive dissociation.

With compounds which are strongly dissociated in the solid state, the maximum in a fusion or transformation curve need not correspond with the composition of the compound, and the same limitation holds also for other properties, such as conductivity and its temperature-coefficients. The maximum (or minimum) under such conditions is only an indication of the existence of a compound. These deductions are not applicable to compounds which are stable over a wide range of temperature without taking the components into solid solution. There is no symmetrical relationship between solubility curves and the curves of homogeneous equilibrium.

D. F. T.

The Artificial Coloration of Spherolites with Helicoidal Winding (Tartrates and Hydrogen Malates). PAUL GAUBERT (*Compt. rend.*, 1918, **167**, 368—370).—The spherolites are easily obtained, artificially coloured, if a solution of the substance containing some methylene-blue is evaporated as a thin layer on a glass plate. The temperature and velocity of crystallisation have a great influence on the production of these spherolites. The methylene-blue is in the crystalline state in the spherolites. Good results were obtained with ammonium hydrogen malate and the hydrogen tartrates of sodium, ammonium, rubidium, and thallium.

W. G.

Chemical Studies on Physiology. V. "Soluble" and "Insoluble" Colloids, Genuine and Spurious Jellies, Protoplasma and Cell Permeability. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **88**, 232—282).—A theoretical paper. The authors distinguish between "soluble" and "insoluble" colloids. They assume that in all cases of solution the solute forms combinations with many molecules of the solvent, and solutions with all stages between molecularly dispersed and colloidally dispersed particles exist. The latter form "soluble" colloids. In contradistinction to these, "insoluble" colloids exist, which owe their dispersion to the adsorption of substances on their surface with great affinity for water. To the latter class proteins belong. The view of the authors on these substances has been expressed in previous papers. Gelatin is regarded as a mixture of polypeptides polymerised by means of calcium salts. Jellies are formed from colloids with great power of combining with water, and come into existence when the whole of the water in the system is accumulated on the surface of the colloidal particles. Corresponding with the "soluble" and "insoluble" colloids are the "genuine" and "spurious" jellies, the former of which only are reversible. The authors discuss the application of their ideas to the problems of cell permeability and metabolism.

S. B. S.

Chemical Equilibria in the Reduction and Cementation of Iron. RUDOLF SCHENCK (*Zeitsch. Elektrochem.*, 1918, **24**, 248—255).—A general résumé of work on the iron—carbon, iron—carbon monoxide, and similar equilibria.

J. F. S.

Propagation of Flame through Tubes of small Diameter.

WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1918, **113**, 656—666).—In continuation of previous experiments on the speed of the "uniform movement" during the propagation of flame in mixtures of methane and air, observations have been made with tubes of small diameter. The results obtained show the increased cooling effect of the walls of the tube as its diameter is decreased, in that the apparent limits of inflammability are narrowed considerably. It is also found that the speeds of the flames tend towards a constant value of about 35 cm. per second as the limiting mixtures are approached, and it is supposed that this represents the slowest speed at which continued propagation of flame ("uniform movement") is possible in mixtures of methane and air.

Experiments made on the propagation of flame through tubes open at both ends, the mixture of methane and air in the tube being ignited near one end of the tube, show that the distance travelled before vibrations are set up which lead to the extinction of the flame depends on the length and diameter of the tube and on the composition of the mixture. The distance increases with the length and the diameter of the tube and diminishes as the percentage of methane in the mixture approaches that corresponding with the maximum speed of propagation of the flame (9·5—10% methane). In consequence of these relations, it follows that a length of tube the diameter of which is small enough to prevent the passage of flame in the mixture which corresponds with maximum speed of flame propagation may fail to do so when the mixture contains a smaller proportion of methane.

Further experiments described have reference to the propagation of flame through short lengths of narrow brass tubes from vessels filled with inflammable mixtures. The explosion vessels, consisting of tubes 2 cm. in diameter and of different lengths, contained 10% mixtures of methane and air. The mixture was ignited near the closed end, and the speed with which the flame reached the narrow brass exit tube was varied by varying the length of the explosion tube. The results obtained with brass tubes from 4 to 8 mm. in diameter, and with explosion vessels varying in length from 10 to 40 cm., show clearly that the increased speed of propagation of the flame reduces considerably the protection which is afforded by the narrow brass exit tubes.   H. M. D.

Relative Activities of Methyl, Ethyl, and n-Propyl Iodides with Sodium a- and β-Naphthoxides.

HENRY EDWARD COX (T., 1918, **113**, 666—674).—The rate of the reactions between the alkyl iodides and sodium a- and β-naphthoxide in ethyl-alcoholic solution has been measured at 40°. For equivalent quantities of the reacting substances, the course of the reaction is satisfactorily represented by the equation for a bimolecular change. The magnitude of the velocity-coefficient increases, however, with the dilution of the original solution. The coefficient k_v for dilution v can be expressed in the form $k_v = k_1 + a \log v$. This equation holds for

ethyl and n-propyl iodides at least as far as $v = 40$. For methyl iodide, the relation holds up to $v = 10$ in the case of sodium a-naphthoxide and to $v = 7$ for the β-naphthoxide. At higher dilutions, methyl iodide reacts more rapidly than would be expected from the empirical formula.

The reactivity of the iodides decreases with increase in the weight of the alkyl group. Sodium a-naphthoxide is more reactive than the β-compound. H. M. D.

The Law of Action of Sucrase: Hypothesis of an Intermediate Compound. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1918, **167**, 338—341).—When the sucrose is in excess with respect to the sucrase, the weight x of sugar hydrolysed in a time t is proportional to the quantity of sucrase n and independent of the initial concentration a of the sucrose. The velocity of inversion, at first constant, diminishes until the excess of sucrose has disappeared, at which point the value of the quotient $(dx/dt)/(a-x)$ remains constant. If, on the other hand, the sucrase is in excess with respect to the sucrose, the rate of inversion is proportional to a and independent of n, and the velocity of hydrolysis, constantly decreasing, is such that the quotient $(dx/dt)/(a-x)$ remains constant throughout. These results are in accord with Brown's hypothesis as to the formation of a compound between the sugar and the enzyme (compare T., 1902. **81**, 373). W. G.

Influence of Foreign Substances on the Activity of Catalysts. V. Experiments with Palladium Hydrosol in the Presence of the Hydroxides of Iron, Copper, and Zinc. C. PAAL and WILHELM HARTMANN (*Ber.*, 1918, **51**, 894—906. Compare this vol., ii, 303).—Ferric hydroxide is peptised to a certain extent by sodium protalbinate, but the amount of iron taken up is lessened by the addition of sodium hydroxide. Freshly precipitated ferric hydroxide does not hinder the catalysis of mixtures of hydrogen and oxygen by palladium hydrosol, protected by sodium protalbinate, nor does it suffer reduction under such conditions.

Cupric hydroxide is taken up by sodium protalbinate to a fairly considerable extent, and free sodium hydroxide enhances the peptisation. More concentrated cupric hydroxide hydrosols than have hitherto been described can therefore be made (compare A., 1906, ii, 358). Freshly precipitated cupric hydroxide lowers the activity of palladium hydrosol towards hydrogen and oxygen mixtures, but large quantities would be necessary to spoil the catalyst entirely. With colloidal cupric hydroxide, however, the activity of the catalyst actually increases for a time, but then falls off rather rapidly. In both cases the falling off is not regular, for after some time a slight recovery sets in, followed again by further loss of activity.

Zinc hydroxide is also peptised by sodium protalbinate   This

depresses the activity of palladium hydrosol during the first hour of an experiment to about half the normal, but a remarkable recovery then sets in, and the catalyst actually becomes slightly more active than usual, although it still contains colloidal zinc hydroxide.   J. C. W.

Inhibition of Foaming. CYRUS H. FISKE (*J. Biol. Chem.*, 1918, **35**, 411—413).—From a consideration of the manner of action of substances which inhibit foaming, the author draws the conclusion that the chief properties contributing to the efficiency of an organic liquid as a foam inhibitor are as follows: high surface activity, high surface tension, high interfacial tension, low solubility, and low volatility. A substance which possesses these characteristics is *iso*amyl *iso*valerate (or a mixture of this substance with *iso*amyl alcohol). To prepare the reagent, 28 c.c. of anhydrous *iso*valeric acid, 30 c.c. of *iso*amyl alcohol, and 1 c.c. of concentrated sulphuric acid are boiled together for one hour under a reflux condenser. The resulting ester is carefully freed from acid by shaking with sodium carbonate and then well washed with water. It may be used at once or after distillation. An alternative method of preparation is to oxidise *iso*amyl alcohol with potassium dichromate and sulphuric acid; the product contains some *iso*valeraldehyde, which can, however, be removed by shaking with sodium hydrogen sulphite solution.   H. W. B.

A Simple Gas Generator. BRUCK (*Chem.-techn. Woch.*, 1917, **1**, 246; from *Chem. Zentr.*, 1918, i, 690).—A small generator working on the same principle as Kipp's apparatus is constructed from a wide glass tube by fitting it internally near its closed end with a perforated shelf of rubber or similar material. The neck of the tube is fitted with a cork; through this passes a test-tube to which has been sealed concentrically a narrow glass tube, this glass tube reaching through the shelf to the bottom of the wide containing tube. For the generation of hydrogen, zinc is placed on the shelf and hydrochloric acid introduced at the mouth of the test-tube; the acid flows through the test-tube and its extension into the end of the wider tube, and then rises until it passes through the shelf to the zinc.   D. F. T.

Aspirator. J. M. JOHLIN (*J. Ind. Eng. Chem.*, 1918, **10**, 632).— A large glass bottle, serving as the reservoir, is closed by a cork carrying three tubes; one of these is the inlet or outlet for the gas, another is used as a siphon for emptying the water from the bottle when this is full, whilst water is admitted through the third tube so that the gas may be forced out. The water enters through a narrow jet in a wide tube fitted at the top of the third tube, the wide tube being provided with a side-tube which carries off any excess of water.   W. P. S.

Safety Valve. E. RITTENHOUSE (*J. Ind. Eng. Chem.*, 1918, **10**, 633).—A short length of glass tube has a small bulb at its lower

end and a narrow central tube is sealed to the inner wall and extends almost to the bottom of the bulb; a globule of mercury in the bulb seals the lower end of the central tube. When this piece of apparatus is inserted in a hole in a cork closing a flask, air may enter through the central tube, bubble through the mercury, and enter the flask through a small opening in the wall of the tube above the bulb. The valve is useful when ammonia is being distilled and absorbed in standard acid, air is admitted to the flask during any temporary decrease in pressure in the latter, thus preventing the standard acid from being drawn into the flask. Vapours cannot escape through the valve outwards owing to the mercury rising in the central tube.   W. P. S.

Filtration Apparatus. F. Härtel (*Zeitsch. Nahr. Genussm.*, 1918, **35**, 444—445).—An apparatus for filtration under reduced pressure consists of a rectangular specimen jar without a neck and having a square, overlapping lid. The jar is laid on its side, and in the upper side are bored two holes, one for receiving the stem of a funnel or filter tube and the other a tube provided with a three-way tap and connected with a pump. The vessel (beaker, flask, etc.) in which the filtrate collects is placed in the jar beneath the stem of the funnel. The apparatus enables the filtrate to be collected directly in a vessel, in which it may be subjected to any further treatment, and transference from a filter-flask is avoided.
                                                            W. P. S.

Ultra-filtration of Small Quantities of Liquid by Centrifugal Force. D. J. DE WAARD (*Arch. Néerland. Physiol.*, 1918, **2**, 530—533).—The apparatus consists of a thick glass tube about 60 cm. long and 1 cm. bore separated from a similar tube, closed at its distal end, by a nickel disk pierced with openings about 2 mm. in diameter. The membrane is placed on the disk, and then the tubes are pressed firmly on to the disk by means of a screw cap and collars attached to the tubes. The whole apparatus now resembles a test-tube divided into an upper and a lower portion by the disk supporting the membrane. A minute hole is pierced in the side of the lower tube just below the collar to allow of the escape of air. The liquid to be filtered is poured on the membrane, and the apparatus then placed in a centrifugal machine. If the number of revolutions per minute is about 3000, the filtration pressure is about 6 atmospheres per sq. cm. The membrane may be of animal origin, or prepared from celloidine or other material by Walpole's method. During centrifugalisation, the lower tube should be protected by an outer tube of copper, the intervening space being filled with oil.   H. W. B.

New Form of Ultra-filter. Some of its Uses in Biological and Synthetic Organic Chemistry. PHILIP ADOLPH KOBER (*J. Amer. Chem. Soc.*, 1918, **40**, 1226—1230).—Quantitative dialysis has hitherto been impossible on account of the extreme

dilution of both filtrate and residue caused by the dialysing water. Through the discovery that all semipermeable membranes pervaporate (Kober, A., 1917, ii, 295), the difficulties of ultra-filtration by dialysis have been completely overcome. An apparatus, consisting essentially of a dialyser with automatic water supply connected by a siphon to a pervaporator, is figured and described. Its action depends on pervaporating both the dialysate and the diffusate solutions during dialysis, whereby quantitative dialysis is rendered possible.

The author gives a few examples showing that in biological or synthetic work humus material or highly coloured by-products, which cannot be removed by charcoal, are rapidly or completely removed by ultra-filtration. [See also *J. Soc. Chem. Ind.*, October.]
C. S.

Device to ensure Tight Connections between Glass and Rubber Tubing. C. C. KIPLINGER (*J. Ind. Eng. Chem*, 1918, **10,** 631).—A piece of stout string is tied round the joint and is tightened by slipping a piece of metal wire between the string and rubber, and twisting the wire until the string is quite tight; the ends of the wire are then bent round the tube.   W. P. S.

Inorganic Chemistry.

Enrichment of Iodine during its Purification. Francesco Lenci (*Boll. chim. farm.*, 1918, **57**, 121—123).—In the purification of iodine, sublimation removes most of the cyanogen iodide, which sublimes first, and also the bromine and moisture, and sublimation in presence of potassium iodide gets rid of chlorine and bromine. Loss of iodine during the purification may be avoided by treatment based on the results obtained by Tarugi (this vol., ii, 203). [See, further, *J. Soc. Chem. Ind.*, 579a.]   T. H. P.

The Theory of Transmission of Oxygen. Ed. Justin-Mueller (*J. Pharm. Chim.*, 1918, [vii], **18**, 17—18).—Certain metallic salts, particularly copper salts, behave as anaeroxydases, and the authors conclude that these substances have secondary valencies having the power to take up oxygen and to transmit it at once under suitable conditions. Anaeroxydases and copper salts behave alike in the oxidation of guaiacum resin in the presence of hydrogen peroxide.   W. P. S.

Reduction of Sulphuric Acid by Carbon Monoxide. Jar. Milbauer (*Chem. Zeit.*, 1918, **42**, 313—315).—At 250°, sulphuric acid is reduced by carbon monoxide according to the equation

$H_2SO_4 + CO = CO_2 + SO_2 + H_2O$; about 25 mg. of sulphur dioxide are produced per hour when carbon monoxide is passed at the rate of 0·6 litre per hour through a layer of sulphuric acid 9·5 cm. in height. The reaction proceeds as long as the strength of the sulphuric acid does not fall below 91%, and is accelerated by the presence of certain catalysts, such as palladium, iridium, mercury, selenium, silver, gold, tin, etc. Platinum, osmium, and copper sulphate do not affect the rate of the reaction. W. P. S.

Preparation and Testing of Pure Arsenious Oxide. ROBERT M. CHAPIN (*J. Ind. Eng. Chem.*, 1918, **10**, 522—524).— Ordinary arsenious oxide is boiled for about one hour with a quantity of water insufficient to dissolve the whole of it, the solution filtered while hot, the filtrate concentrated until arsenious oxide begins to precipitate, and the solution again filtered. The separated oxide is tested for antimony by dissolving a portion in ammonia, adding hydrogen sulphide, boiling the mixture, and then cooling in ice-water; a turbidity is obtained if more than 0·15% of antimony trioxide is present, and in such case the arsenious oxide must be treated further as described. The purification depends on the fact that antimony, if present, is absorbed almost completely by the solid arsenious oxide which remains undissolved in the aqueous solution. The final crystallisation of the pure arsenious oxide is best made from a slightly hydrochloric acid solution, and the product is then sublimed. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

Silicon Hydrides. V. Decomposition of Silicon Hydrides by Water. Action of Hydrogen Bromide on Monosilane. ALFRED STOCK and CARL SOMIESKI (*Ber.*, 1918, **51**, 989—996. Compare A., 1916, ii, 319; this vol., ii, 110, 111).—In the first communication on the silanes, it was reported that they suffer decomposition into silicic acid and hydrogen when left for a few hours in contact with water. It is now found that this reaction is largely conditioned by the alkalinity of the glass apparatus, for in quartz vessels, or with slightly acidified water practically no change takes place during several days.

This stability of the hydrides may be made use of in analysing mixtures of the three gases, monosilane, hydrogen bromide, and bromomonosilane. The last-named gas reacts immediately with water to form the gas disiloxane and hydrobromic acid, thus: $2SiH_3Br + H_2O = (SiH_3)_2O + 2HBr$. After two or three hours, the new gas reacts further to give hydrogen, thus: $(SiH_3)_2O + H_2O = SiO_2 + 3H_2$. If the volume of the mixture is a c.c., the volume after the initial contraction is b c.c., and the final volume after the production of hydrogen is c c.c., then $c - b$ gives the volume of SiH_3Br and $a - b - \frac{1}{2}(c - b)$ the volume of HBr.

From the point of view of carbon chemistry, a remarkable reaction of the silicon hydrides has now been discovered. Monosilane, for example, reacts very readily with hydrogen bromide in the

presence of aluminium bromide, according to the equations
$SiH_4 + HBr = SiH_3Br + H_2$, $SiH_4 + 2HBr = SiH_2Br_2 + 2H_2$, etc.   In
one experiment, which is fully described, 207 c.c. of monosilane and
188·8 c.c. of hydrogen bromide were heated for three hours at 100°
in a sealed tube of 700 c.c. capacity, on the walls of which a little
aluminium bromide had been deposited by sublimation, when 86·7
c.c. of monosilane, 52·5 c.c. of SiH_3Br, and 67·8 c.c. of SiH_2Br_2 were
obtained from the product, practically all the hydrogen bromide
having disappeared. This method is consequently better than
direct bromination for the preparation of the lower bromides.

The apparatus employed is described in another paper (see this
vol., ii, 353).   J. C. W.

Melting Points of Cristobalite and Tridymite. J. B.
FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1918, [iv], **46**,
417—426).—Cristobalite prepared by heating clear quartz crystals
for 144 hours at 1300—1400° melts at 1710°±10°.

Tridymite grains selected from the cristobalite mass were con-
verted into cristobalite at 1667—1677° without melting. Two speci-
mens of natural tridymite (one from Nevada and one from Mexico)
both melted sharply at 1670°±10°. The results confirm those of
Fenner (A., 1913, ii, 133), showing that the region of stability of
cristobalite is above that of tridymite. [See, further, *J. Soc. Chem.
Ind.*, 546A.]   A. B. S.

A Supposed Fusion of Carbon by O. Lummer. M. LA ROSA
(*Gazzetta*, 1917, **47**, ii, 19—31).—The author criticises Lummer's
conclusions (*Verflüssigung der Kohle*, etc., Braunschweig, July,
1914), and directs attention to some of his earlier experiments.
                                                T. H. P.

Residual and Extinctive Atmospheres of Flames. THOMAS
FRED ERIC RHEAD (*J. Soc. Chem. Ind.*, 1918, **37**, 274—278T).—
Experiments have been made with the flames of a number of
different gases to determine the amount of oxygen in (1) the "resi-
dual atmosphere," that is, the atmosphere in which the flame,
burning in a limited supply of air, becomes extinguished, and (2)
the "extinctive atmosphere," that is, the mixture of oxygen and
nitrogen which is just unable to support combustion of the gas.

The residual atmospheres of flames of the hydrocarbons methane,
propane, butane, and pentane were found to contain from 15·6%
to 16·4% of oxygen, the value increasing gradually with the mole-
cular weight. For cyanogen, the value found was 15·3%, for
carbon monoxide 10·2%, and for hydrogen 5·7%. The oxygen con-
tent of the residual or extinctive atmosphere depends primarily on
the rate of diffusion of the combustible gas into the atmosphere and
on the complexity of the combustion process. Hydrogen, with a
high rate of diffusion, a simple reaction, and a high initial rate of
flame propagation in air, therefore leaves an atmosphere with a
low oxygen content.

For the examination of the extinctive atmospheres, a novel experimental method was devised, consisting in feeding a flame with a mixture of air and nitrogen which could be varied at will with considerable nicety. The mixture which just extinguished the flame was taken as the extinctive atmosphere. The oxygen content in the case of the hydrocarbons methane to pentane was found to be practically constant at 16·3—16·6%, with a constant speed of the gas stream and of the current of air–nitrogen mixture. It was found, however, that the flame would continue to burn in an atmosphere containing less oxygen when the atmosphere was supplied at a greater speed. Coal gas behaves differently from a pure gas, on account of the widely different extinctive atmospheres of its two principal constituents, hydrogen and methane. Experiments on a mixture of these gases showed that in the presence of an atmosphere of low oxygen content the hydrogen burns preferentially. The methane under these conditions acts mainly as a diluent, and this accounts for the observation that in the case of coal gas the oxygen content of the extinctive atmosphere is diminished by increasing the speed of the gas stream.   E. H. R.

The Ternary System—Sodium Sulphate, Ammonium Sulphate, and Water. The Utilisation of Nitre Cake for the Production of Ammonium Sulphate. HARRY MEDFORTH DAWSON (T., 1918, **113**, 675—688).—An account is given of the equilibrium relations in the system Na_2SO_4–$(NH_4)_2SO_4$–H_2O at temperatures between $-20°$ and $100°$. The characteristic features of the system, which are illustrated by diagrams of a somewhat novel type, are largely determined by the formation of the ternary compound $Na_2SO_4,(NH_4)_2SO_4,4H_2O$, which may exist in contact with solutions at any temperature between $-16°$ and $59·3°$. Below $-16°$, the double salt, in contact with solution, is decomposed, with the formation of Glauber's salt and ammonium sulphate, and above $59·3°$ it decomposes with the formation of the anhydrous simple salts. Other invariant temperatures are $-19·5°$, at which Glauber's salt, ammonium sulphate, and ice co-exist in equilibrium with saturated solution, and $26·5°$, at which the saturated solution is in equilibrium with Glauber's salt, anhydrous sodium sulphate, and the double salt.

The curves which show the influence of temperature on the composition of the solutions saturated with respect to two solid phases are distinguished by the fact that the solutions saturated with respect to Glauber's salt and the double salt show a rapid diminution in the ammonium sulphate concentration and a rapid increase in the sodium sulphate concentration as the temperature rises from $-16°$ to $26·5°$. On the other hand, solutions saturated with respect to anhydrous sodium sulphate and the double salt show a decrease in the sodium sulphate concentration and a remarkably rapid increase in the ammonium sulphate concentration as the temperature rises from $26·5°$ to $59·3°$.

Between $-16°$ and $20°$, the double salt is decomposed by water

with the separation of Glauber's salt, and between 41·5° and 59·3° it is similarly decomposed with the separation of anhydrous sodium sulphate. These intervals of temperature represent the lower and upper transition intervals.

In virtue of the considerable differences in the values of the ratio of ammonium sulphate to sodium sulphate in the saturated solutions at high and low temperatures, it is possible to separate these salts by crystallisation under suitably controlled conditions. A method has been devised in which solutions of appropriate concentration are cooled to a temperature of about −10°, when Glauber's salt separates out, the mother liquors being subsequently evaporated at about 100° when pure ammonium sulphate is, deposited until the ratio of ammonium sulphate to sodium sulphate in the hot solution has fallen to a value much smaller than that characteristic of the mother liquor from the crystallisation process.

H. M. D.

Composition of Lime–Sulphur Solutions. O. B. WINTER (*J. Ind. Eng. Chem.*, 1918, **10**, 539—545).—Lime–sulphur solution which has been prepared from ordinary commercial lime and sulphur, and has been kept for several days, does not contain any appreciable amount of hydrogen sulphide, calcium hydrosulphide, calcium hydroxyhydrosulphide, or the corresponding salts of other metals; free calcium hydroxide is not present. When, however, an excess of lime has been used in preparing the lime–sulphur solution, or when the latter has been diluted with lime-water, free calcium hydroxide may be present for a time, but gradually disappears. The addition of magnesium sulphate to lime–sulphur solution produces a slight increase in the monosulphide sulphur and sulphide sulphur contents, whilst the thiosulphate sulphur content is not affected; the magnesium replaces calcium, magnesium polysulphide being formed and calcium sulphate crystallising from the solution. Free sulphur does not appear to be present in lime–sulphur solution, and any sulphur which separates is derived from the higher polysulphides. The orange-red crystals which separate from concentrated lime–sulphur solution have the composition $2CaO,CaS_3,11H_2O$, but it is improbable that they exist in this form in the solution. [See, further, *J. Soc. Chem. Ind.*, October.]

W. P. S.

Influence of the Temperature of Burning on the Rate of Hydration of Magnesium Oxide. EDWARD DE MILLE CAMPBELL (*J. Ind. Eng. Chem.*, 1918, **10**, 595—596).—When magnesite is ignited at or below 1100°, the resulting magnesium oxide, when immersed in water, is hydrated completely within three months; if the ignition is made at 1450°, only 70% of the magnesium oxide is hydrated in six years. These results show that materials containing free magnesium oxide, if ignited at temperatures approaching that used in the production of Portland cement, will not be hydrated completely, even when immersed continuously in

water, until after the lapse of twenty years or more. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

The Ternary Systems Lead–Bismuth–Silver and Lead–Gold–Silver. MASAHARU GOTO (*J. Coll. Eng. Tokyo*, 1918, **9,** 63—114).—In the system lead–gold–silver, no ternary eutectic occurs. The temperature of the eutectic falls continuously from 350° for the lead–silver alloys to 208° for the lead–gold ones. The presence of gold reduces the power of silver of holding lead in solid solution. No compound is present. In the lead–bismuth–silver system, a ternary eutectic occurs containing 0·2% Ag, 43·6% Pb, and 56·2% Bi, which melts at 120°. Solid solutions occur in a narrow area around the silver corner of the diagram. F. C. TH.

Compounds of Lead Fluoride and Chloride with Lead Phosphate. M. AMADORI (*Atti R. Accad. Lincei*, 1918, [v], **27,** i, 143—148).—The results obtained in the thermal study of the system lead fluoride–lead phosphate (A., 1913, ii, 216) were vitiated, owing to the presence in the phosphate both of a slight excess of lead oxide and apparently also of traces of another substance the nature of which was not determined. The examination of this system has now been repeated, the lead phosphate used being prepared from the calculated quantities of lead oxide and pyrophosphate, the latter itself being obtained by precipitation of lead nitrate with disodium hydrogen phosphate. The results show that fused mixtures of lead orthophosphate and fluoride form, on solidification, the compound $Pb_3(PO_4)_2,PbF_2$, which solidifies at 1098°. This compound and the analogous chloropyromorphite, $Pb_3(PO_4)_2,PbCl_2$, solidifying at 1156°, correspond in composition with the mineral pyromorphite and undergo no transformation during cooling. Each of these compounds exhibits little if any miscibility with its components. T. H. P.

Action of Hydrogen Sulphide on Mercuric Bromide. GIAMBATTISTA FRANCESCHI (*Boll. chim. farm.*, 1918, **47,** 221—223). —The addition of a few drops of an alcoholic solution of hydrogen sulphide to an alcoholic solution of mercuric bromide produces slight milkiness, mercurous bromide and sulphur being formed: $H_2S + 2HgBr_2 = Hg_2Br_2 + S + 2HBr$. Addition of a greater proportion, but not an excess, of the hydrogen sulphide solution causes the precipitation of the canary-yellow double salt,
$$2HgS.HgBr_2 \ (?Hg[S \cdot HgBr]_2),$$
whilst when excess is added, black mercuric sulphide is precipitated. The successive reactions are represented by the equations: (1) $H_2S + 2HgBr_2 = Hg_2Br_2 + S + 2HBr$; (2) $H_2S + 3Hg_2Br_2 + 3S = 2(2HgS.HgBr_2) + 2HBr$; (3) $H_2S + HgS,HgBr_2 = 2HgS + 2HBr$.
T. H. P.
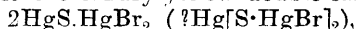
Recovery of Molybdic Acid. W. H. LYNAS (*Met. and Chem. Eng.*, 1918, 169).—The following method is suggested for recover-

ing molybdic acid from the filtrates from phosphorus estimations. To the boiling filtrates from 3500 c.c. of ammonium molybdate solution, 200 grams of commercial sodium phosphate are added. The precipitate is washed by decantation and dried on a sand-bath; it is then dissolved in ammonia and the phosphorus precipitated by the addition of magnesium nitrate solution and filtered. The volume of the filtrate is made up to 3500 c.c. by the addition of 1900 c.c. of 1:1 nitric acid. [See, further, *J. Soc. Chem. Ind.*, October.]   F. C. Th.

Bismuth Tellurides. II. M. AMADORI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 131—134. Compare A., 1915, ii, 783).—The author has subjected to thermal investigation that part of the Bi–S–Te system comprising the compositions of other natural sulpho-tellurides, that is, $Bi-Bi_2Te_3-Bi_2S_3$. It is found that the single components, Bi, Bi_2S_3, and Bi_2Te_3, and the compound, Bi_2S_3,Bi_2Te_3, separate out from fused mixtures either in the pure state or in simple eutectic mixtures; there is no formation of new compounds and no miscibility relationships between these substances. No phenomena are observed which are attributable to the formation of substances analogous to tetradimite, grunlingite, or joseite.   T. H. P.

Mineralogical Chemistry.

Anhydrite in the Boulders carried by the Lava of Stromboli. G. PONTE (*Atti R. Accad. Lincei*, 1917, [v], **26**, ii, 348—350).—The mineral has the percentage composition:

CaO.	SO_3.	BaO.	SrO.	SiO_2.	Fe_2O_3.
42·09	57·79	0·04	0·06	traces	0·02

R. V. S.

Analytical Chemistry.

Calculation of Analytical Results. J. GROSSFELD (*Chem. Zeit.*, 1918, **42**, 389—391).—Tables are given showing the equivalents and analytical factors of a large number of elements, inorganic compounds, organic compounds, and acids, sugars, alkaloids, etc.   W. P. S.

Graphic Methods of Analysis. HANS GRADENWITZ (*Chem. Zeit.*, 1918, **42**, 368).—The system of curves suggested previously by the author (this vol., ii, 245) merely indicates the application of this method of analysis; no claim is made for priority or for the particular trustworthiness of the diagrams given.
W. P. S.

Graphic Methods of Analysis. WA. OSTWALD (*Chem. Zeit.*, 1918, **42**, 367—368).—The author recommends the use of Gibb's triangular scheme for plotting the curves employed in the estimation of the composition of ternary mixtures; this system is simpler and more trustworthy than that described by Gradenwitz (this vol., ii, 245, and preceding abstract).
W. P. S.

Use of the Dipping Refractometer. WYATT W. RANDALL (*J. Ind. Eng. Chem.*, 1918, **10**, 629—630).—In using the immersion refractometer, the author has found that the temperature of the liquid under examination rises slightly when the metal cup containing the liquid is attached to the instrument, probably due to the conduction of heat from the air to the cup through the metal parts of the instrument. Untrustworthy readings are therefore obtained. This heating does not take place when small beakers are used in place of the metal cups.
W. P. S.

New Form of Colorimeter. JOSEPH C. BOCK and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1918, **35**, 227—230).—The new colorimeter differs from the Duboscq instrument in having only one plunger, the light from a mirror being thrown partly through the glass containing the liquid the colour intensity of which it is required to measure, and partly through a cell containing a known depth of liquid of standard colour.
H. W. B.

Use of the Interferometer in Gas Analysis. F. M. SEIBERT and W. C. HARPSTER (*U.S. Bureau of Mines, Tech. Paper*, No. 185, 1918, 18 pp.).—A description of the application of the Rayleigh interferometer to gas analysis, especially in special work necessitating frequent analyses. Using a gas chamber 1 metre long, the precision is equivalent to the ordinary volumetric gas analysis made over mercury.

The accuracy of the measurements depends largely on the length of the gas chambers, and the refractive index must be measured with great precision for accurate work. The percentage error made in determining one component of a mixture depends also on the choice of a comparative gas, and it is found better to calibrate the instrument empirically against some exact analytical method.

In order to obtain an accuracy of 0·02%, when using as a gas of comparison the gas that predominates in the mixture, the absolute refraction coefficients should differ by about 0·0001; therefore the greater the difference of the coefficients of absolute refraction, the

greater is the accuracy of the method. The gases compared must be dry and at the same temperature. [See, further, *J. Soc. Chem. Ind.*, 608A.]   C. A. K.

Electrical Conductivity Recorder for Salinity Measurements.

E. E. WEIBEL and A. L. THURAS (*J. Ind. Eng. Chem.*, 1918, **10**, 626—627).—The apparatus described gives a continuous record of the salinity or density of a solution by the measurement of its electrical conductivity; it may be used for the concentration of brines and other salt solutions, and also many other substances the composition of which is constant during changes in concentration. Two electrolytic cells are used and are connected with a suitable alternating current galvanometer and a recorder. Temperature compensation is effected by placing both cells, which are in the two arms of a Wheatstone bridge, in a uniform temperature-bath or directly in the solution under examination.

W. P. S.

A New Physico-chemical Volumetric Method.

RENÉ DUBRISAY (*Ann. Chim.*, 1918, [ix], **9**, 25—48).—The method described for determining the acidity of a solution is based on the observation and measurement of the tension at the surface of separation of two non-miscible liquids. A definite volume of vaselin oil mixed with 2% of oleic acid is allowed to flow slowly into a known volume of the liquid under examination from a jet just plunged into it, and the number of drops formed is counted. This is repeated after the addition of known volumes of standard alkali, and it is found that there is a sudden rise in the number of drops formed at the point of neutralisation. The vaselin oil may be replaced by a solution of stearic acid in benzene.   W. G.

Decanting.

H. TILLISCH (*J. Ind. Eng. Chem.*, 1918, **10**, 631).— The time required for a precipitate to settle is shortened considerably if the test-tube is inclined at an angle of 45°.   W. P. S.

Neutralisation of Hydrogen Peroxide by Sodium Borate.

J. CAMBE and H. DIACONO (*J. Pharm. Chim.*, 1918, [vii], **18**, 12—17).—The presence of small quantities of hydrofluosilicic acid or hydrofluoric acid in hydrogen peroxide inhibits the formation of a red coloration when the peroxide is treated with phenolphthalein and an excess of sodium borate; freshly prepared hydrogen peroxide, which contains "active oxygen," also fails to give a red coloration when treated with an excess of sodium borate in the presence of phenolphthalein. Other indicators are not affected by the above-mentioned substances.   W. P. S.

Estimation of Chlorine in Presence of Silicates.

G. BRUHNS (*Zeitsch. angew. Chem.*, 1918, **31**, [i], 156).—In estimating chlorine in mixtures containing silicic acid, it is unnecessary

to render the silica insoluble and separate it by filtration. Mohr's method of titrating the chlorine with silver nitrate is trustworthy provided that the liquid be made neutral to phenolphthalein by means of nitric acid, and any gelatinous silicic acid be finely distributed throughout the liquid.   C. A. M.

Source of Error in Bunsen's Method for the Estimation of Peroxides, Chlorates, etc. E. RUPP (*Zeitsch. anal. Chem.*, 1918, **57**, 226—230).—When manganese dioxide, potassium chlorate, etc., are estimated by distilling the substance with hydrochloric acid, collecting the distillate in potassium iodide solution, and titrating the liberated iodine, the results obtained are from 0·5% to 2% too low. The error varies with the conditions of the distillation, and is due to reaction between chlorine and water vapour, hydrochloric acid and oxygen being formed. Fairly trustworthy results are, however, obtained if potassium iodide is added to the distillation mixture and the iodine then distilled, collected, and titrated. In some cases, where the hydrochloric acid is too concentrated, iodine in small amount is liberated from the potassium iodide by the action of the acid.   W. P. S.

Estimation of Sulphuric Acid and Barium as Barium Sulphate. Z. KARAOGLANOW (*Zeitsch. angew. Chem.*, 1918, **31**, 160).—A criticism of an investigation recorded by Winkler (*Zeitsch. angew. Chem.*, 1917, **30**, 301—303) on the gravimetric estimation of sulphuric acid and barium. The author has shown recently (this vol., ii, 47) that potassium salts influence the results, and that the presence and concentration of the hydrochloric acid, the time of precipitation, temperature, all have an effect on the precipitation of the barium sulphate. There is no evidence that barium hydrogen sulphate is formed during the precipitation.
W. P. S.

The Microchemical Estimation of Nitrogen. IVAR BANG (*Biochem. Zeitsch.*, 1918, **88**, 416—419).—A reply to some criticisms of Schollema and Hitterschy (*ibid.*, 1917, **84**, 354, 371).
S. B. S.

Use of Sodium Sulphate in the Kjeldahl-Gunning Method. C. T. DOWELL and W. G. FRIEDEMAN (*J. Ind. Eng. Chem.*, 1918, **10**, 599—600).—The authors find that sodium sulphate (either anhydrous or an equivalent quantity of the crystallised salt) is as effective as is potassium sulphate in the digestion part of the Kjeldahl-Gunning method.   W. P. S.

Estimation of Ammonia in Urine. A. LECLÈRE (*Compt. rend. soc. biol.*, 1917, **80**, 959—962; from *Physiol. Abstr.*, 1918, **3**, 262).—By distilling urine with lithium carbonate, ammonia is rapidly and quantitatively liberated. The hydrolysing action on

urea and amino-acids is slight, so that only a small correction is necessary.   S. B. S.

Ammonia and Nitric Nitrogen Estimations in Soil Extracts and Physiological Solutions. B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1918, **10**, 600—605).—Ammonia nitrogen is estimated by the aeration method at the ordinary temperature in the presence of magnesium oxide or sodium carbonate; the ammonia is absorbed in acid towers, and the contents of the latter are distilled subsequently with magnesium oxide in the usual way. The residual liquid in the aeration flask is then acidified with sulphuric acid, heated, cupric hydroxide added, the mixture filtered, the filtrate boiled for thirty minutes with the addition of sodium hydroxide, and the nitrate reduced with Devarda's alloy, the resulting ammonia being estimated by distillation. [See, further, *J. Soc. Chem. Ind.*, October.]   W. P. S.

The Estimation of Nitrites. F. DIENERT (*Compt. rend.*, 1918, **167**, 366—367).—The method is based on the reaction $NaNO_2 + 2HI = NaI + I + NO + H_2O$. Three flasks, (1) containing 50 c.c. of 4% potassium iodide, (2) containing 10 c.c. of N-sulphuric acid, (3) containing the solution of the nitrite, are connected in the order mentioned, and carbon dioxide passed through them until all air is displaced. The contents of (1) are then driven over into (2), and this mixture in turn into (3). Ten c.c. of a 20% solution of ammonium carbonate are then added, and the free iodine titrated by means of $N/70$-arsenious acid, of which 1 c.c. $= 0.2$ mg. of nitrous nitrogen. Care must be taken to avoid the entrance of oxygen into flask (3) until the liquid has been made alkaline by the addition of the ammonium carbonate.   W. G.

Colorimetric Estimation of Phosphoric Acid in Potable Water. P. N. VAN ECK (*Pharm. Weekblad*, 1918, **55**, 1037—1040). —The hydrazine sulphate employed in Riegler's colorimetric method for estimating phosphoric acid can be replaced by stannous chloride, the same blue coloration being produced.   A. J. W.

Estimation of Zeolitic Silicic Acid in Soils. K. K. GEDROITZ (*Reprint*, pp. 400—406).—The method commonly used in Russian laboratories for the estimation in soils of so-called zeolitic silicic acid, that is, silicic acid liberated when the soil is treated with concentrated hydrochloric acid in the hot, is tedious, and the author now describes a new method, which is rapid and does not necessitate the use of large platinum dishes. The results obtained by this method approximate closely to those given by the old method.   T. H. P.

Pressure Method for the Estimation of Carbon Dioxide in Carbonates. W. H. CHAPIN (*J. Ind. Eng. Chem.*, 1918, **10**, 527—529).—The carbonate is dissolved in dilute hydrochloric acid contained in a flask of known capacity; the flask is provided with

a small mercury manometer, and the weight and percentage of the carbon dioxide are calculated from the change in pressure. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

The Bisulphate Method of Estimating Radium. Howard H. Barker (*J. Ind. Eng. Chem.*, 1918, **10**, 525—527).—In this method, the mineral is fused and boiled with a mixture of sodium and potassium hydrogen sulphates, and the emanation is passed into the ionisation chamber of an electroscope. Readings of the rate of discharge are made three hours after the introduction of the gas. When the mineral under examination contains thorium, the gas cannot be transferred directly to the electroscope during fusion, but must be collected in a gas burette to allow the thorium emanation to decay. [See, further, *J. Soc. Chem. Ind.*, October.] W. P. S.

Methods of Estimating Potassium. A. Vürtheim (*Chem. Weekblad*, 1918, **15**, 827—842).—A critical survey of the literature of the estimation of potassium. A. J. W.

Estimation of Zinc in Zinc Dust. L. A. Wilson (*Eng. and Min. J.*, 1918, **106**, 334—336).—A sample of zinc dust with ferrous sulphate and a piece of platinum foil are placed in a small conical flask connected through a three-way tap with a measuring tube. The whole system is then filled with liquid saturated with hydrogen at the temperature of experiment, the flask and connecting tube containing water and the measuring tube 10% sulphuric acid. The addition of sulphuric acid through a separating funnel causes evolution of hydrogen, and if any fine particles of zinc are carried over, solution is completed by the acid in the measuring tube. Finally, water is run through the separating funnel to force the hydrogen into the measuring tube, and, after levelling, the volume is read off and corrected. C. A. K.

Microchemical Reaction for Manganese. J. B. Menke (*Chem. Weekblad*, 1918, **15**, 868—869).—A drop of ammonia containing cyanuric acid gives with manganese sulphate a precipitate of manganous hydroxide. After a few minutes, or immediately on boiling, colourless, unstable needles of high polarising power separate from the mixture. A. J. W.

Rapid Method for the Estimation of Iron in small Quantities of Blood. Louis Berman (*J. Biol. Chem.*, 1918, **35**, 231—236).—The iron held in combination in the blood is liberated by the action of concentrated hydrobromic acid, whilst the organic matter is destroyed by potassium permanganate and the iron simultaneously oxidised to the ferric condition. The resulting solution is mixed with a solution of ammonium thiocyanate in water and acetone, and the colour compared with that of a standard iron solution similarly treated. The ordinary ashing process is

thus eliminated, and the estimation requires only 0·040 c.c. of blood, and may be completed in ten to fifteen minutes.

<div align="right">H. W. B.</div>

Estimation of Chromium in the Presence of Iron. K. SCHORLEMMER (*Collegium*, 1918, 145—149).—Iron salts must be removed previous to the estimation of chromium by means of thiosulphate. The solution is treated with hydrogen peroxide, heated, then cooled, and reoxidised by the addition of a further quantity of hydrogen peroxide; the ferric hydroxide is collected, dissolved in acid, twice oxidised with hydrogen peroxide, again collected, and the filtrate added to the first filtrate. The chromium is then estimated in the solution. A further treatment of the ferric hydroxide with hydrogen peroxide may be necessary if much iron is present.

<div align="right">W. P. S.</div>

Analysis of Molybdenum Ores containing Copper. W. HOEPFNER and O. BINDER (*Chem. Zeit.*, 1918, **42**, 315).—Small quantities of copper in an ammoniacal solution of molybdic acid cannot be precipitated by the addition of ammonium sulphide, since copper is soluble to the extent of 0·015 gram (or more) per 100 c.c. of the sulphide solution. To effect the separation of the copper, the ammoniacal solution should be acidified with sulphuric acid and the copper deposited electrolytically after the addition of nitric acid.

<div align="right">W. P. S.</div>

Ilsemannite. H. F. TANCY (*Met. and Chem. Eng.*, 1918, (186).—Ilsemannite is a blue compound of molybdenum soluble in water to which the formula $MoO_2,4MoO_3,6H_2O$ is usually given. The molybdenum, occurring as MoO_2, may be determined by extracting the ore with hot water, adding to the extract 25% by volume of hydrochloric acid and its own bulk of ether. The mixture is shaken and the layers separated, the aqueous layer being again treated with ether and the ethereal solutions combined. This ether extract is washed ten times with 10 c.c. of hydrochloric acid diluted with 25 c.c. of water to remove iron. The blue compound is titrated with $N/100$-permanganate in a sulphuric acid solution. The total molybdenum present is determined by fuming the solution with strong sulphuric acid, diluting it with water, and adding sodium hydroxide. A precipitate of the hydroxides of manganese and iron is filtered off, the filtrate acidified with 2·5% sulphuric acid, and passed while hot through a Jones reductor.

<div align="right">F. C. TH.</div>

Estimation of Tungsten and Vanadium in the Presence of Titanium. G. FENNER (*Chem. Zeit.*, 1918, **42**, 403).—To separate tungsten from titanium in a mineral, the latter is fused with sodium peroxide, cooled, the fused mass boiled for a few minutes with water, and the solution then filtered; the titanium remains insoluble, whilst the tungsten passes completely into the filtrate. This method cannot be used for the separation of vanadium from titanium, since the greater part, if not all, of the vanadium remains insoluble. In this case, the mineral, after silica

has been removed by treatment with hydrofluoric acid and sulphuric acid, is fused with sodium pyrosulphate, the fused mass dissolved in dilute sulphuric acid, the solution filtered, and the filtrate treated with hydrogen peroxide until a distinct coloration has developed, an excess of the peroxide being avoided. Ammonium fluoride is then added; this destroys the yellow colour of the titanium compound, but does not affect the reddish-brown colour of the vanadium compound. After the yellow colour due to iron salts has been removed by the addition of phosphoric acid, the vanadium is estimated colorimetrically, using a standard prepared under the same conditions and as far as possible with the same quantities of reagents. W. P. S.

Quantitative Analysis of Vanadium Compounds with the Aid of Carbon Tetrachloride. PAUL JANNASCH and HENRY E. HARWOOD (*J. pr. Chem.*, 1918, [ii], **97**, 93—137).—The application of carbon tetrachloride as a reagent for quantitative analysis (Jannasch and others, A., 1913, ii, 876; 1910, ii, 1076; 1909, ii, 728, 767; 1908, ii, 685; 1907, ii, 864) is extended by its use for the estimation of vanadium in its compounds. The vanadium compound in a silica boat enclosed in a silica tube is heated in a current of carbon dioxide and carbon tetrachloride vapour, the resulting vanadium chlorides being collected by passage into dilute nitric acid and water successively. The vanadic acid solution thus obtained is reduced to vanadyl sulphate, the amount of which can then be estimated volumetrically with potassium permanganate. [See also *J. Soc. Chem. Ind.*, October.] D. F. T.

Application of Rapidly Rotating Metallic Reductors in the Estimation of Vanadic Acid. F. A. GOOCH and W. SCOTT (*Amer. J. Sci.*, 1918, [iv], **46**, 427—436).—The reduction of vanadic acid in the presence of dilute sulphuric acid may be effected quickly by the aid of rapidly rotating anodes of silver or copper in an electrolytic cell or by a rapidly rotating cylinder of zinc, over-reduction being corrected by the addition of silver sulphate, which automatically forms vanadium tetroxide. The completion of the reduction is indicated by the appearance of precipitated silver in the solution. The reduced liquid is boiled to coagulate the silver, filtered, diluted, again heated to boiling, and titrated with potassium permanganate. The correction applied is variable when an electrode of commercial copper is used, but an electrode of silver plated with copper from a solution of copper sulphate, free from iron, is satisfactory. When zinc is the reducing agent, the results are comparable only if the volume and temperature of the solution, the relative size of the zinc cylinder, and its rate of rotation are kept constant. A. B. S.

Electroanalysis of Bismuth without Platinum Electrodes. PELAYO POCH (*Anal. Fis. Quim.*, 1918, **16**, 520—533).—An account

of experiments on the estimation of bismuth in solution in nitric, tartaric, sulphuric, and acetic acids, and in ammoniacal solution. In each case, the estimation was carried out with platinum electrodes, with a platinum anode and a copper cathode, with a platinum cathode and an iron or graphite anode, and with a copper cathode and an iron or graphite anode.   A. J. W.

The Copper Method for Estimating Glycerol. F. L. Weiss (*Chem. Weekblad*, 1918, **15**, 862—868).—There is no compound of copper and glycerol of constant composition, but the proportion of copper depends on four factors: (1) The proportion of glycerol in the solution, the amount of copper increasing with the glycerol. (2) Any rise of temperature, which lowers the proportion of copper, especially in very dilute solutions. (3) The degree of dilution of the liquid. (4) The concentration of the free alkali.
          A. J. W.

The Estimation of Phenol in "Cresylic Acid." J. J. Fox and M. F. Barker (*J. Soc. Chem. Ind.*, 1918, **37**, 265—268т).—For the estimation of phenol in commercial 'cresylic acid' by the method previously described (A., 1917, ii, 513), a number of additional details are given. In place of ether, benzene may be used for getting rid of tar oils and bases, but since benzene is obstinately retained by the solution of the tar acids in sodium hydroxide solution, this solution must be heated sufficiently strongly before acidification to expel all the benzene. Benzene may also be used in place of ether to extract the tar acids after acidification, the washing and drying being carried out as described before. The neutral oils and bases may also be removed by dissolving the tar acids in sodium hydroxide solution and steam distilling, but care must be taken that the sodium hydroxide is in sufficient excess to prevent any tar acids, particularly *o*-cresol, being carried over with the steam.

A short method has been devised for determining whether a sample of 'cresylic acid' contains more than about 5% of phenol. The dried tar acids are fractionally distilled in the standard apparatus described, and the fraction distilling up to 210° is collected and redistilled. The portion boiling up to 202° is collected, and if this is less than 5% the sample is satisfactory. If it is more than 5%, it is again distilled, and the fraction boiling up to 195° is collected and the phenol estimated by a specific gravity determination.

A bibliography of papers dealing with phenol and cresol estimations and separations is appended.   E. H. R.

Chemical Diagnosis of Picric Jaundice. Possible Simulation of Bile Pigments in the Urine. Domenico Ganassini (*Boll. chim. farm.*, 1918, **57**, 161—167).—The author describes methods of detecting the simulated catarrhal jaundice caused by the ingestion of picric acid by individuals (in Italy) wishing to

escape military service, these methods being modifications of Le Mithouard's reaction (*Presse médical.*, 1916, No. 27, 475), the tri-aminophenol reaction (compare Rodillon, A., 1915, ii, 805), and Derrien's diazo-reaction (*Presse médical.*, 1915, No. 35, 285) for the detection of picric acid derivatives in the urine. It is pointed out that Le Mithouard's reaction is given also by Martius-yellow and by naphthol-yellow S, the latter being a harmless colour allow-able in food products; these colouring matters do not, however, respond to the other two reactions mentioned.

Only in exceptional cases of picric jaundice may the picramic acid in the urine be accompanied by bile pigments, this being so especi-ally when large doses of picric acid have been ingested. It is found that the possibility exists of simulating the presence of bile pig-ments in a urine which does not contain them, for instance, by addition of either a pinch of antipyrine mixed with a trace of alkali nitrate or a very small quantity of Congo-red; a method is given for detecting this fraud, which may be practised to render the jaundice more certain. T. H. P.

Identification and Estimation of Potassium Guaiacol-sulphonate. SAMUEL PALKIN (*J. Ind. Eng. Chem.*, 1918, **10,** 610—612).—Potassium guaiacolsulphonate as used in medicine is usually mixed with gums, resins, alkaloids, etc. To detect the presence of the sulphonate, the sample is treated with dilute hydro-chloric acid, filtered, and a portion of the filtrate tested for sulphates before and after oxidation with sodium peroxide (in the acid solution); any increase in the quantity of sulphate after oxidation indicates the presence of a sulphonate. Another portion of the filtrate is rendered alkaline and treated with a drop of diazotised *p*-nitroaniline; a deep red coloration, changing to yellow when acidified, denotes the presence of guaiacolsulphonate. In the absence of much organic matter, a portion of the sample may be distilled with the addition of phosphoric acid and sodium chloride; the filtrate gives a green coloration with ferric chloride, and, when rendered ammoniacal, reduces silver nitrate. Potassium guaiacol-sulphonate may be estimated from the amount of sulphuric acid formed when it is oxidised by repeated evaporation with bromine and nitric acid. W. P. S.

Estimation of Acetic Acid by Distillation with Phosphoric Acid. W. FAITOUTE MUNN (*J. Ind. Eng. Chem.*, 1910, **10,** 550—552).—For the estimation of acetic acid in calcium acetate residues, etc., the sample is distilled with the addition of dilute phosphoric acid, and the distillate is collected in a receiver con-taining an excess of standardised barium hydroxide solution. A current of air free from carbon dioxide is drawn through the apparatus during the distillation, and dilute phosphoric acid is admitted to the distillation flask at the same rate as that at which the liquid distils. When the distillation is completed (this requires

about ninety minutes), the contents of the receiver are titrated with $N/10$-hydrochloric acid, using phenolphthalein as indicator; this gives the excess of barium hydroxide. If any barium carbonate has formed, due to the presence of carbonates in the sample, the barium carbonate is dissolved by adding $N/1$-hydrochloric acid in slight excess and then titrating the excess with $N/1$-sodium hydroxide solution, using methyl-orange as an external indicator. Allowance is made for the quantity of carbonate thus found. [See, further, *J. Soc. Chem. Ind.*, October.]   W. P. S.

The Detection of d-Glycuronic Acid and other Acids with similar Behaviour by the Naphtharesorcinol Reaction. A. W. VAN DER HAAR (*Biochem. Zeitsch.*, 1918, **88**, 205—212).— An application of Neuberg and Saneyoshi's modification of Tollens's reaction, as applied to plant products. The substance is first hydrolysed with 5% sulphuric acid, the mixture is then neutralised with barium hydroxide, and concentrated after filtration. Lead acetate is then added, and, after filtration, basic lead acetate; the glycuronate is contained in the precipitate thus produced, and this is then heated with 10 c.c. of 10% hydrochloric acid and 100 mg. of naphtharesorcinol for one minute. After cooling to 50°, benzene is added, and if glycuronic acid is present, this on shaking takes up a violet pigment, which gives a characteristic D-band of the spectrum.   S. B. S.

Estimation of Phthalic Anhydride in Crude Phthalic Acid. CHARLES R. DOWNS and CHARLES G. STUPP (*J. Ind. Eng. Chem.*, 1918, **10**, 596—598).—The sample is volatilised from a small glass capsule, and the volatilised phthalic anhydride collected in a tube containing cotton wool, the lower end of this tube being inserted in the neck of the capsule. The capsule is heated at 220°, and a current of air drawn through the apparatus during the operation. The cotton wool is then removed from the tube, boiled with an excess of standard sodium hydroxide solution for thirty minutes, the solution then treated with an excess of standard acid, again boiled, and titrated, using phenolphthalein as indicator. Each c.c. of $N/10$-sodium hydroxide solution is equivalent to 0·0074 gram of phthalic anhydride. The non-volatile residue remaining in the capsule may also be weighed. [See, further, *J. Soc. Chem. Ind.*, October.]   W. P. S.

Dropping-point Apparatus for the Examination of Fats, Waxes, and Bitumens. F. DUPRÉ (*Chem. Zeit.*, 1918, **42**, 398. Compare Ubbelohde, A., 1905, ii, 658).—The substance to be tested is placed in a small metal nipple which is attached to the bulb of a thermometer so that the lower part of the bulb is immediately above the surface of the substance. The thermometer is suspended in a test-tube, which is immersed in a heating-bath heated to about 20° below the probable dropping point of the

substance, and the temperature is raised at the rate of 1° per minute until a drop of the melted substance falls from the nipple.

W. P. S.

Method for Estimating Citral. A Modification of the Hiltner Method. C. E. PARKER and R. S. HILTNER (*J. Ind. Eng. Chem.*, 1918, **10**, 608—610).—Some samples of lemon and orange oils and extracts yield a blue or green coloration when treated with *m*-phenylenediamine hydrochloride, thus limiting the applicability of Hiltner's method, which depends on the formation of a yellow coloration. The addition of oxalic acid, however, inhibits the production of the blue or green coloration, and it is recommended that the reagent be prepared as follows: One gram of *m*-phenylenediamine hydrochloride and 1 gram of crystallised oxalic acid are dissolved separately in 80% alcohol, the solutions are mixed, diluted to 100 c.c. with 80% alcohol, treated with Fuller's earth, and filtered.

W. P. S.

Detection of Acetone. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1021—1029).—Vanillin can replace salicylaldehyde in Frommer's test for acetone (*Berl. Klin. Wochenschr.*, 1902, **42**, 1005) with similar results. The presence of acetaldehyde or formaldehyde is prejudicial.

A. J. W.

Estimation of Acetone. ALLAN J. FIELD (*J. Ind. Eng. Chem.*, 1918, **10**, 552).—Messenger's volumetric method, depending on the formation of iodoform, was found to be untrustworthy; the use of arsenious acid in place of thiosulphate for the titration (compare Vaubel and Scheuer, A., 1905, ii, 291) yielded no advantage. Robineau and Rollin's method as modified by Kebler (*J. Amer. Chem. Soc.*, 1897, **19**, 316) is the most trustworthy for the estimation of acetone; the results are not affected by the presence of alcohol or by differences in the time of shaking.

W. P. S.

Method for the Separation and Quantitative Estimation of the Lower Alkylamines in the Presence of Ammonia. F. C. WEBER and J. B. WILSON (*J. Biol. Chem.*, 1918, **35**, 385—410).—The *total volatile nitrogen* is first estimated by distillation of the alkaline solution containing ammonia and the amines into 0·05N-acid, and titration of the excess of acid with 0·02N-alkali, using methyl-red as the indicator.

For the estimation of the *total amines*, a volume of the original solution containing an amount of total volatile nitrogen equivalent to from 40 c.c. to 60 c.c. of 0·05N-acid is placed in a 500 c.c. volumetric flask, diluted with water to within 20 c.c. of the mark, and treated with 10 c.c. of an alkaline mixture composed of equal parts of 20% sodium hydroxide and 30% sodium carbonate solutions. After making to the mark, 0·1 gram of yellow oxide of

mercury is added for each c.c. of $0.1N$-acid equivalent to the total
volatile nitrogen. The flask is covered with a black cloth and
shaken for one hour. The solution is then filtered through a
cotton filter under pressure, and two 200 c.c. portions of the filtrate
are distilled into 25 c.c. of $0.05N$-acid. The acid neutralised is
equivalent to the amines present, from which the total amines
may be calculated. The difference between the total volatile
nitrogen and the total amines represents the *ammonia* nitrogen.

The distillate containing the total amines is acidified with 0.5 c.c.
of concentrated sulphuric acid and evaporated to 35 c.c. It is
transferred to a 50 c.c. flask and diluted with water to the mark.
The *monoamines* are now estimated in 10 c.c. in the Van Slyke
amino-nitrogen apparatus, using the mixing bulb of the large size
apparatus and the measuring burette of the micro-apparatus. The
remaining 40 c.c. are transferred to a 200 c.c. flask and treated
with 20 c.c. of a saturated solution of sodium nitrite and 10 c.c.
of glacial acetic acid. The liquid is shaken from time to time to
remove as much gas as possible, and, after an hour, a drop of
phenolphthalein indicator is added and 30 c.c. of a 20% sodium
hydroxide solution. On mixing, the solution should remain acid;
if it begins to turn red, a few drops of acetic acid are added. After
a few hours, 15 c.c. to 20 c.c. more of the sodium hydroxide solu-
tion are added, and it is distilled into 25 c.c. of $0.05N$-sulphuric
acid. It is titrated back as before with $0.02N$-alkali, using methyl-
red as indicator. The acid used is equivalent to the *triamines*.
The *diamines* may be estimated by difference, or by the follow-
ing method. To the distillate containing the triamine (and also
the diamine in the form of nitrosoamine) 10 c.c. of concentrated
hydrochloric acid and a few grams of granulated zinc are added,
and when hydrogen is being evolved freely it is placed over a
small flame and heated to boiling. The solution is decanted from
the remaining zinc, which is washed with three 10 c.c. portions
of water. After addition of a drop of phenolphthalein and about
10 grams of sodium hydroxide, the product is distilled into 25 c.c.
of $0.05N$-acid, and titrated back as before. The acid used is
equivalent to the sum of the diamines and triamines present.

The method appears to give accurate results, and may be
employed in the analysis of fish products, putrid flesh, bad
sausages, biological fluids, etc.   H. W. B.

Evaluation of Hexamethylenetetramine Tablets. W. O
EMERY and C. D. WRIGHT (*J. Ind. Eng. Chem.*, 1918, **10**,
606—608).—A portion of the sample is boiled under a reflux
apparatus with dilute hydrochloric acid, and the solution is then
made up to a known volume. An aliquot portion of this solution
is treated at $0°$ with alkaline potassium mercuric iodide solution
(a modified Nessler reagent); the formaldehyde is oxidised to a
formate, and an equivalent amount of metallic mercury is pre-
cipitated. The mixture is then acidified with acetic acid, and an
excess of $N/10$-iodine solution added; the iodine combines with

the mercury, and the excess of iodine is titrated with thiosulphate solution. [See, further, *J. Soc. Chem. Ind.*, October.]

W. P. S.

Abnormalities in the Formol Titration Method. S. L. JODIDI (*J. Amer. Chem. Soc.*, 1918, **40**, 1031—1035).—An explanation is given of the abnormalities which sometimes render untrustworthy Sörensen's formaldehyde titration method of estimating amino-acids, polypeptides, etc The function of the formaldehyde is to convert the basic nitrogen in the molecule into a neutral group, so that the carboxyl group can be accurately titrated; in the case of simple amino-acids, $NH_2 \cdot R \cdot CO_2H$, containing only amino- and carboxyl groups, the reaction is

$$NH_2 \cdot R \cdot CO_2H + CH_2O = CH_2 : N \cdot R \cdot CO_2H + H_2O ;$$
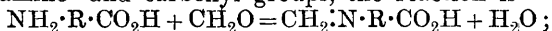
the group $CH_2 : N \cdot$ is neutral, and the resulting monobasic acid contains no groups modifying its acidity. Proline, however, contains an imino-group, and reacts with formaldehyde to give methyleneproline containing the group $: N \cdot CH_2 \cdot N :$, which is still somewhat basic, with the result that the formaldehyde method gives too low results. The same holds for hydroxyproline. The product from formaldehyde and histidine also contains the group $: N \cdot CH_2 \cdot N :$, and the estimation is therefore low, but the result is better than in the case of proline, probably owing to the acidic nature of the azole nucleus. Tryptophan has not yet been estimated by Sörensen's method, but in view of the presence of an imino-group, it seems safe to predict that the result will be low. In the case of lysine, the method gives low results, although an accurate result would be expected, since the molecule contains, apart from the two amino-groups, no groups which could affect the carboxyl group; the discrepancy is attributed to the distance of the ω-amino-group from the carboxyl group. C. S.

Analysis of Calcium Cyanamide containing much Dicyanodiamide and Urea. E. HENE and A. VAN HAAREN (*Zeitsch. angew. Chem.*, 1918, **31**, 129—131).—A solution of the cyanamide, dicyanodiamide, and urea is prepared in the usual way, and an aliquot portion, containing about 0·2 gram of nitrogen, is diluted to 200 c.c. and treated with 20 c.c. of 10% silver nitrate solution and 30 c.c. of 10% potassium hydroxide solution; the precipitate, which contains all the cyanamide and dicyanodiamide and some of the urea, is washed, mixed with 150 c.c. of water, dissolved in the minimum quantity of nitric acid, diluted to 200 c.c., and 100 c.c. of this solution are treated with 2 c.c. of silver nitrate solution and 15 c.c. of potassium hydroxide solution. The precipitate, which now contains all the cyanamide and dicyanodiamide, is collected and the nitrogen in it determined by Kjeldahl's method. In another portion of the original solution, the cyanamide is precipitated by means of silver nitrate and ammonia, and the nitrogen determined in the precipitate; the difference between this and the first nitrogen determination gives the dicyanodiamide nitrogen.

The urea nitrogen is found from the difference between the sum of the cyanide and dicyanodiamide nitrogen and the total nitrogen in the sample.   W. P. S.

[Estimation of] Creatinine in Blood. I. CHERTKOV (*Rev. méd. suisse romande*, 1917, **37**, 748; from *Physiol. Abstr.*, 1918, **3**, 247).—Protein is precipitated by trichloroacetic acid; to the filtrate, sodium hydroxide and picric acid are added, and the creatinine is estimated colorimetrically.   S. B. S.

Estimation of Theobromine. W. O. EMERY and G. C. SPENCER (*J. Ind. Eng. Chem.*, 1918, **10**, 605—606. Compare A., 1914, ii, 825).—A method for the estimation of theobromine, either alone or mixed with sodium acetate and sodium salicylate, depends on the formation of its periodide, $C_7H_8O_2N_4,HI,I_4$. A quantity of 0·1 gram of the sample (with an equivalent quantity of sodium acetate in the case of theobromine alone) is dissolved in 2 c.c. of glacial acetic acid, 5 c.c. of hot water are added, and the solution is transferred to a 100 c.c. flask containing 50 c.c. of $N/10$-iodine solution; 20 c.c. of saturated sodium chloride solution and 2 c.c. of concentrated hydrochloric acid are then added, and, after about eighteen hours, the mixture is diluted to 100 c.c., filtered, and the excess of iodine titrated in an aliquot portion of the filtrate. [See, further, *J. Soc. Chem. Ind.*, October.]   W. P. S.

Method for making Electrometric Titrations of Solutions containing Protein. JOHN C. BAKER and LUCIUS L. VAN SLYKE (*J. Biol. Chem.*, 1918, **35**, 137—145).—The apparatus consists of a wide-mouthed bottle, holding about 400 c.c., provided with a cork stopper containing perforations through which the several parts or connexions pass into the bottle. The hydrogen electrode, made of platinum foil, is suspended in a special manner inside the bell-shaped end of the tube carrying hydrogen, and is so arranged that it can be lowered into or drawn out of the solution titrated. Other parts are (*a*) a glass tube admitting the titration reagent from a burette into the solution titrated, (*b*) special stirring apparatus, (*c*) a tube for introducing additional reagents, (*d*) a tube containing potassium chloride, and, in addition, other pieces of apparatus required to measure the hydrogen-ion concentration.

In operating, the solution under examination is placed in the bottle, and hydrogen passed in, the electrode being above the solution. The stirrer being in motion, the electrode is lowered into the solution, electric connexions are made, equilibrium is established, and then the titration reagent run in. Readings of the *E.M.F.* are made once a minute until constant, and the titration is then continued. The apparatus is designed to prevent local chemical action at the point where the reagent enters the solution under titration.   H. W.

General and Physical Chemistry.

Spectrochemistry and Determination of the Constitution of Tautomeric Compounds. K. VON AUWERS (*Annalen*, 1918, **415**, 169—232).—Brühl showed more than thirty years ago that molecular refraction and dispersion can be utilised to differentiate between enolic and keto-modifications, but the determination in recent times of the composition of keto-enol mixtures by chemical means has frequently led to results which are quite opposed to Brühl s views. The author has undertaken a series of researches, of which this is the first, to ascertain how far spectrochemistry in its present state can be applied to investigations of desmotropic compounds.

With the difference in structure represented by the scheme ·CO·CHR· ⇌ ·C(OH):CR· correspond constant differences in the molecular refraction and dispersion of such magnitudes that a trustworthy decision between the two structures can be made when only homogeneous substances are in question; also the percentage composition of mixtures of simple enols and ketones, for example, a simple unsaturated alcohol and the isomeric aldehyde or ketone, can be ascertained with satisfactory accuracy by the refractometric method, especially if the specific refraction and dispersion are employed instead of the molecular magnitudes. Errors arise, however, and false conclusions may be drawn when certain groups are present in the molecule. For example, in β-diketones, β-ketonic acids, etc., occur the systems ·CO·CHR·COR′ and

OH·C:CR·CR′:O.

The former is spectrochemically normal, but the latter, containing a conjugate system of linkings, exhibits an abnormal increase of the refraction, and still more so of the dispersion. Almost the only possible way of overcoming this difficulty is the calculation of the magnitude of the exaltations by means of known regularities. Eisenlohr and Auwers (A., 1910, ii, 365 ; 1911, ii, 781) have shown that the magnitudes of the specific exaltations of the refraction and dispersion remain practically constant in compounds containing the same conjugate system. so that 'normal values' of the specific exaltations can be recorded. Unfortunately, this regularity is not equally sharp in all classes of substances, possibly on account of experimental error or of lack of purity of the compounds examined. It is necessary, therefore, to determine more accurately than hitherto the normal values of the specific exaltations for the conjugate system CH:CH·CR:O and ·CH:CH·C(OR):O, and to ascertain the influence of disturbing substituents on these values. By means of the numbers so obtained, the theoretical values of the molecular refraction and dispersion of the enols could be calculated, and thus the foundations laid for a more trustworthy determination c he equilibrium proportions of enolic and keto-modifications by

means of the optical constants. The author then discusses the values obtained for series of hydroxymethylene compounds and their ethers and esters, and draws the conclusion that a trustworthy calculation of the real molecular refraction and dispersion of enols is possible at the present time only in a few cases in which specially favourable comparison material is available. The following substances have been examined. The percentages are calculated from the spectrochemical data, and the figures in brackets are the percentages found by Meyer's bromine method. Ethyl diacetoacetate, percentage of keto-enol 100 (90—100); acetylacetone, enol 69% (76); methylacetylacetone, keto-enol 38% and 31% in two different preparations (31); ethylacetylacetone, keto-enol about 27%; ethyl acetylmalonate, enol 70% (64); methyl benzoylacetate, enol 25% (16·7); ethyl benzoylacetate, enol 29% (29); ethyl α-benzoylbutyrate, enol at most a few units per cent.; methylbenzoylacetone, enol 22% (6).

The spectrochemical constants (density and refractive indices for the α-, D-, β-, and γ-lines) have been determined of the following hydroxymethylene compounds and their ethyl ethers and acetates; γ-keto-β-methyl-Δ⁰-penten-α-ol; hydroxymethylenepinacolin (*ethyl* ether, b. p. 103—104°/16 mm.; *acetate*, rhombohedral plates, m. p. 44—45°, b. p. 118—118·5°/16 mm.); 2-hydroxymethylene-*cyclo*hexanone (*ethyl* ether, b. p. 128·2—128·4°/16 mm.; *acetate*, b. p. 142—143°/14 mm.); 2-hydroxymethylenementhone; ethyl β-acetoxyacrylate; ethyl β-hydroxy-α-methylacrylate; ethyl hydroxymethyleneacetoacetate; ethyl hydroxymethylenemalonate. The constants are also given for the following diketones and ketonic esters: acetylacetone (and the O-methyl and -ethyl ethers); methylacetylacetone; dimethylacetylacetone; ethylacetylacetone; methylbenzoylacetone (and the O-methyl ether); β-methoxy-β-amylacrylic acid and its methyl ester; ethyl β-ethoxy-β-amylacrylate; ethyl O-acetylacetoacetate; ethyl diacetoacetate; methyl benzoylacetate and the ethyl ester; ethyl ethylbenzoylacetate.   C. S.

Atomic Refraction and Atomic Dispersion of Quadrivalent Lead, Deduced from the Saturated Lead Tetraalkyls. GERHARD GRÜTTNER and ERICH KRAUSE (*Annalen*, 1918, **415**, 338—362).—Hitherto, the atomic refraction of quadrivalent lead, 17·87 for the red hydrogen line (n^2 formula), has been deduced from only one compound, lead tetra-ethyl. Since it is known that the atomic refraction of silicon, deduced from the silanes, varies between 7·0 and 8·0, it is very desirable that the value for lead should be recalculated, and for this purpose the numerous lead tetra-alkyls prepared by the authors in 1916 and 1917 are well suited, since they are colourless, stable liquids. The values of the atomic refraction and dispersion of quadrivalent lead depend on the number of carbon atoms in the molecule, and increase from the C_4 to about the C_{12} compounds. The values calculated from the simple, completely symmetrical lead tetra-alkyls (PbR_4) increase

regularly with the molecular weight. The authors are decidedly of opinion that there are no constant values. The atomic refraction (H_α line) increases from 17·07 for the C_4 compound to 18·16 for the C_{11} compounds, and the atomic dispersions increase from 1·43 to 1·75 (H_γ—H_α), and from 0·87 to 1·05 (H_β—H_α).

Certain regularities in the b. p.'s, densities, and refractions and dispersions of lead alkyls and silicon alkyls are recorded.　C. S.

Atomic Number and Frequency Differences in Spectral Series. HERBERT BELL (*Phil. Mag.*, 1918, [vi], **36**, 337—347).— It has been previously shown by Rydberg and by Kayser and Runge that for elements in the same periodic group the wave-number differences between the components of doublet and triplet series are approximately proportional to the squares of the atomic weights. This relation has been further examined, the atomic weights being replaced by the atomic numbers.

By plotting the square root of the wave-number difference against the atomic number, straight lines are obtained corresponding with the equation $\sqrt{\nu} = m(N - N_0)$, in which N is the atomic number of the element and m and N_0 are constants. ' In the first group, the elements lithium, sodium, potassium, rubidium, and cæsium fall on one straight line, for which $m = 0\cdot4447$ and $N_0 = 1\cdot875$, whilst potassium, copper, silver, and gold fall on a second straight line, for which $m = 0\cdot8117$ and $N_0 = 9\cdot619$. There is thus a twofold collinearity in the first group of the periodic table, and this feature is again met with in the second group.

The linear relation between the square root of wave-number differences and atomic numbers has also been found to hold for the members of other groups in the periodic arrangement.

The logarithmic relation $\log \nu = p \log N + q$, which was suggested by Runge and Precht (A., 1903, ii, 346), does not seem to be in better agreement with the facts than the equation $\sqrt{\nu} = m(N - N_0)$.
　　　　　　　　　　　　　　　　　　　　　　　H. M. D.

Photographic Record of the K-Spectra of Platinum and Iridium. J. E. LILIENFELD and H. SEEMANN (*Physikal. Zeitsch.*, 1918, **19**, 269—271).—The K-spectra of platinum and iridium have been examined with the aid of a new type of spectrograph. The intensity distribution in the spectra and the effect of the interposition of a layer of aluminium, as determined by photometric observations, are shown in the form of curves. The photographs obtained show the existence of rays of shorter wave-length than any which have been previously described.　　　H. M. D.

Spectrum of Cadmium in the Inactive Gases. J. N. COLLIE and H. E. WATSON (*Proc. Roy. Soc.*, 1918, [A], **95**, 115—120).—Making use of tubes fitted with a cadmium cathode and an aluminium anode, and filled with one of the gases helium, argon, neon, or xenon, the authors have observed certain peculiarities in the spectrum of cadmium. The cadmium lines 6438, 5379, 5338, 5086, 4800, 4678, and 4416 were generally seen, but the

intensity of the lines varied with the pressure and current. Thus with helium at a pressure of 40 mm., four of the cadmium lines were visible, and with neon at 60 mm. pressure, two were visible. In many cases, the lines 5379 and 5338 were entirely absent and the individual lines varied considerably with the gas employed. In the case of the lines 5379 and 5338, it was found that with helium at 40 mm. they were scarcely visible, whilst at 5 mm. they were the brightest lines of the spectrum; in argon they only became visible at 2·5 mm., whilst in xenon these two and 4678 were the only lines visible when a weak current was used. Tables of the intensities of the lines in helium at various pressures are given for the current values 5-and 0·5 amperes. The line 5086 behaved in an unusual manner, in that whilst the experimental conditions were constant, it suddenly flared up to an intensity equal to that of the brightest of the other lines and then suddenly vanished. In the case of argon, the lines 6438, 5086, 4800, and 4678 were very bright at 21 mm. pressure. At 3 mm. pressure, only 5086 was to be seen, and 5379 and 5338 did not appear until the pressure was reduced to 2·5 mm. In krypton, the results were indefinite; the same applies to xenon. The heating effect of the cathode is progressive, being least with helium and greatest with xenon.   J. F. S.

Origin of the Line Spectrum Emitted by Iron Vapour in an Electric Tube Resistance Furnace at Temperatures above 2500°. G. A. HEMSALECH (*Phil. Mag.*, 1918, [vi], **36,** 281—296. Compare this vol., ii, 341).—Further observations on the furnace spectrum of iron at high temperatures are described, all of which point to the conclusion that this spectrum is not a purely thermal effect, but is due to the passage of a current through the vapour of the metal. At 2700°, the furnace spectrum is entirely different from the flame spectrum at the same temperature and approaches in character the arc spectrum of the element. Direct evidence has been obtained that a current will readily pass through the vapour in a tube furnace. The line spectrum does not disappear immediately when the heating current is cut off, but is exhibited for some time afterwards, the lines being extinguished gradually. The spectrum emitted after the current is broken does not correspond with the temperature of the cooling vapour. Attempts to obtain a line spectrum under conditions in which electrical action was excluded by the use of a furnace of special design gave a negative result.

The fact that the vapours of copper, silver, and zinc give no line spectrum when subjected to thermo-electric action in the electric tube resistance furnace at 2700° is supposed to be due to the small conductivity of these vapours as compared with that of the vapours of iron, cobalt, and nickel, all of which readily give a line spectrum under the same furnace conditions.

The methods of excitation which give rise to spectral emission in flames, furnace, arc, and spark are severally distinguished and grouped as (*a*) thermal, (*b*) thermo-chemical, (*c*) chemical,

(*d*) thermo-electrical, (*e*) electrical. The observations on iron vapour show that the line spectrum cannot be produced by thermal excitation alone.   H. M. D.

Ionisation and Spectral Emission of Different Elements in the Positive Column. O. HARDTKE (*Ann. Physik*, 1918, [iv], **56**, 383—387).—According to Stark's investigations, the emission of characteristic spectra is associated with positively charged ions. In consequence of differences in the ionising potentials, it is to be expected that when glow discharge takes place through a tube containing several gases, the positive column will show marked differences in the spectral emission at various points. Experiments made with a tube containing mercury, nitrogen, and argon have actually shown a distribution of the spectra of these elements which are in the order to be expected from a consideration of their ionising potentials. In proceeding from the cathode towards the anode end of the positive column, the order in which the characteristic spectra make their appearance is mercury, nitrogen, argon; this is also the order of the positions of maximum intensity of comparable lines. Of the three elements, mercury has the lowest ionisation potential and argon the highest. The distribution of the spectral emission along the positive column is thus found to be dependent on the ionising potentials of the elements concerned.
                                                             H. M. D.

Binuclear Quinones.   Chemical Action of Light. HANS MEYER and ALFRED ECKERT (*Monatsh.*, 1918, **39**, 241—251).—As has already been demonstrated (Meyer and Hofmann, A., 1916, i, 641), dihydroanthracene, when heated, readily decomposes into anthracene and hydrogen, and it is therefore to be expected (Meyer and Hofmann, this vol., i, 383) that the same dissociation should occur under the influence of light. Contrary to the statement of Orndorff and Cameron (A., 1896, i, 176), this substance does undergo chemical alteration when exposed to light from the sun or electric arc, the products being hydrogen and para-anthracene, the latter being formed by the immediate polymerisation of the "nascent" anthracene, which is the primary product; in the presence of substances capable of reacting with the "nascent" anthracene, other products may be obtained. The action of light on anthracene probably also first gives rise to "nascent" anthracene in which the diagonal valency becomes resolved into two free valencies; by these the formation of para-anthracene becomes possible; if oxygen is present, the products are anthraquinone and dihydrodianthrone (compare Luther and Weigert, A., 1905, ii, 785), the latter being formed by the further action of light on anthranol, which represents an intermediate stage of the change. It is already known that solutions of benzoquinone and thymoquinone in ethyl alcohol when subjected to light give rise to acetaldehyde and the corresponding quinol. With anthraquinone, however, the quinol derivative is unstable, and in contact with air

regenerates anthraquinone; it is therefore possible to use anthra-
quinone as a catalyst for the oxidation of ethyl alcohol to acet-
aldehyde in light, the only other product being a small quantity of
an unidentified substance which gives a brown solution in aqueous
potassium hydroxide. In a similar manner, *iso*propyl alcohol can
be oxidised to acetone, but methyl alcohol is very stable and is
recovered completely unchanged, together with the anthraquinone.
This relative stability of methyl alcohol accords well with the earlier
result of Meyer and Hofmann (*loc. cit.*), and may account for
the preponderance of methyl derivatives amongst the naturally
occurring alkyl compounds. 9:10-Dichloro- and 9:10-dibromo-
anthracene are unaffected by light, but 10-bromoanthracene in
alcoholic solution gradually gives rise to anthraquinone and
bromide ions, together with a temporary small deposit of para-
anthracene. If dihydroanthracene in acetic anhydride solution is
submitted to the action of light, the first deposit of para-anthracene
may disappear on prolonged treatment, probably by further oxida-
tion to anthraquinone; anthranyl acetate is obtained as a by-
product, its formation supplying an explanation of the origin of
dihydrodianthrone in the action of light and air on anthracene in
alcoholic solution. Solutions of anthracene in acetic acid, chloro-
form, and methyl sulphate, when illuminated, give the same pro-
ducts, namely, para-anthracene, anthraquinone, and dihydrodi-
anthrone; it was hoped with the aid of methyl sulphate to isolate
anthraquinol in the form of its dimethyl ether, but unfortunately
this compound is sensitive to light, and in acetic acid solution is
rapidly converted into anthraquinone.   D. F. T.

The Wave-length of the Hard γ-Rays of Radium. K. W.
FRITZ KOHLRAUSCH (*Physikal. Zeitsch.*, 1918, **19**, 345—349).—
The wave-length of the very penetrating γ-rays emitted by
radium-*B* and radium-*C* is discussed with reference to the absorp-
tion of the rays in different elements.   H. M. D.

The Electrical Conductivity of Salt Vapours. GERHARD
C. SCHMIDT (*Ann. Physik*, 1918, [iv], **56**, 341—362. Compare
A., 1911, ii, 788; 1913, ii, 747).—Further attempts to obtain
reproducible data for the electrical conducting power of salt
vapours have given negative results, although various forms of
apparatus have been tried with this object in view. The frequently
observed fact that the conductivity first increases and then decreases
has been traced on the one hand to the slow diffusion of the vapour,
and on the other to the caking of the fused salt at the surface,
resulting in a reduced rate of vaporisation. The velocities of the
positive and negative ions have been determined in the case of
cadmium chloride, bromide, and iodide, and of zinc bromide and
iodide. Although the results for these different salts are not com-
parable with one another, they show that the mobility of the
negative ions is in all cases greater than that of the positive ions.
The ionic mobilities are of the same order of magnitude as those

found by previous investigators for the ions produced in the oxidation of phosphorus and for the ions in flame gases at a considerable distance from the flame. The mobility increases with rise of temperature and depends on the average life of the ion in the sense that the mobility is greater the shorter the average life of the ion.
H. M. D.

New Method for the Determination of Conductivity. EDGAR NEWBERY (T., 1918, **113**, 701—707).—Kohlrausch's method for the determination of the electrical conductivity of solutions is criticised, and a method is described which utilises direct current and completely eliminates the effect of polarisation at the electrodes. This method is a simple modification of the method used in the measurement of the resistance of a metallic conductor by observing the fall of potential along it during the passage of a known current. The values obtained for the conductivity of N-solutions of potassium chloride and sulphuric acid at 25° are respectively 0·3% greater and 3·6% less than the values recorded by Kohlrausch. In the case of N-silver nitrate, the two values are very nearly equal.
H. M. D.

Electrical Conductance of Aqueous Phthalate Solutions. HARRISON E. PATTEN, ALFRED J. JOHNSON, and GERALD H. MAINS (*J. Amer. Chem. Soc.*, 1918, **40**, 1156—1162).—In reference to the application of potassium hydrogen phthalate as a standard in acidimetry and hydrogen-ion concentration measurements, the authors have measured the conductivity of its aqueous solutions at 25°. The molecular conductivity (corrected for the conductivity of the solvent) was found to increase from 76·9 at $v=5$ to 153·0 at $v=10,000$. Hydrogen-ion concentration measurements gave $c_H = 1·29 \times 10^{-4}$ at $v=5$ and $c_H = 1·23 \times 10^{-4}$ at $v=10$. The molecular conductivity of normal potassium phthalate is much higher than that of the acid salt, and was found to increase from 184·8 at $v=20$ to 247·0 at $v=5000$.
H. M. D.

Diamagnetism of Hydrogen and the Value of the Magneton. A. E. OXLEY (*Proc. Roy. Soc.*, 1918, [*A*], **95**, 58—61). —On the assumption that the molecules of diamagnetic substances contain magnetic elements arranged in such a way that the molecule is self-compensated, so that the application of a magnetic field produces only a diamagnetic effect, it is calculated that the moment of the magneton in the case of hydrogen is equal to $14·7 \times 10^{-22}$, which agrees closely with the moment for molecules of ferromagnetic and paramagnetic substances ($16·5 \times 10^{-22}$). If each hydrogen atom contains one magneton, the calculated radius of the electron orbit is about 1×10^{-8} cm.
H. M. D.

The Coefficients of Magnetisation of Oxygen and of Nitric Oxide, and the Theory of the Magneton. EDMOND BAUER, PIERRE WEISS, and AUGUSTE PICCARD (*Compt. rend.*, 1918, **167**, 484—487).—The authors have made fresh measurements of

the coefficients of magnetisation of oxygen and nitric oxide by three different methods, the values obtained being: for oxygen, $\chi_{20} = 1 \cdot 077 \times 10^{-4} \pm 0 \cdot 003 \times 10^{-4}$, $\sigma_{O2} = 1 \cdot 587 \times 10^4$; for nitric oxide, $\chi_{20} = 0 \cdot 487 \times 10^{-4} \pm 0 \cdot 0025 \times 10^{-4}$, $\sigma_{NO} = 1 \cdot 033 \times 10^4$. These values are in contradiction with the theory of the magneton, and it is suggested either that oxygen and its compounds are an exception to the general law or that the discrepancies are due to a difference between the kinetic theory and experimental facts.   W. G.

Magnetic Susceptibility of Mixtures of Liquids. ALPHEUS W. SMITH and ALVA W. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 1218—1224).—Quincke's method has been used in the investigation of the magnetic susceptibility of mixtures of acetone and water, acetic acid and water, acetic acid and benzene, and of acetone and ethyl alcohol. Within the limits of experimental error, the results obtained for the four pairs of substances are in agreement with the requirements of the additive law. It is suggested that the magnetic susceptibility may advantageously be used in the analysis of binary mixtures.   H. M. D.

The Causes of Abnormal Boiling Points. A. BERTHOUD (*J. Chim. Phys.*, 1918, **16**, 245—278).—A theoretical discussion in which the author shows that de Forcrand's views as to the relationship of the abnormal boiling points of water, hydrofluoric acid, and ammonia to their heats of formation and their molecular dissymmetry (compare this vol., ii, 107) are not in accord with experimental facts. On the other hand, molecular association has the effect of raising the boiling point, but not to the extent often stated. Calculations founded on the additivity of the constants b and $\sqrt{a}$ (compare van Laar, A., 1916, ii, 610) indicate that, amongst the substances studied, acetic acid is the only one of which the boiling point and the critical temperature can be explained entirely by association. In cases such as those of water, alcohols, and ammonia, another factor intervenes. The critical pressures of the last-named compounds are also too high, and this cannot be explained on the grounds of molecular association. This other factor, which works with the molecular association in causing high boiling points and critical temperatures in the cases of water and the alcohols, lies in the particularly high value of the constant a, independent of the molecular association, in substances containing an –OH group.   W. G.

Freezing Points of Concentrated Solutions and the Free Energy of Solution of Salts. WORTH H. RODEBUSH (*J Amer. Chem. Soc.*, 1918, **40**, 1204—1213).—Recent improvements in the method of determining the freezing points of dilute solutions (Adams, A., 1915, ii, 222) have been made use of in the investigation of concentrated solutions, the relation between the freezing point and the concentration of various aqueous salt solutions having been followed down to the eutectic temperature. The following

data are recorded for the eutectic composition (grams anhydrous salt per 100 of water) and the eutectic temperature: sodium chloride, 30·4, 21·12°; potassium chloride, 24·60, 10·66°; ammonium chloride, 24·50, 15·36°; magnesium chloride, 28·00, 33·50°; calcium chloride, 48·00, 51·0°; potassium bromide, 45·65, 12·60°; sodium nitrate, 62·50, 17·46°; ammonium nitrate, 74·80, 16·67°; ammonium sulphate, 66·40, 18·34°. Temperature measurements were made by the aid of a copper–constantan thermocouple.

The thermodynamic equations required for the calculation of the free energy change which accompanies the formation of solutions of different concentrations are considered and applied to the experimental data for solutions of sodium chloride and potassium chloride.

H. M. D.

Representation of the Properties of Binary Systems.

G. MASING (*Int. Zeitsch. Metallographie*, 1917, **9**, 82—89; from *Chem. Zentr.*, 1918, i, 800—801).—In the graphic representation of the properties of binary systems in relation to the composition, curves of the most peculiar form can, in certain cases, be obtained by a quite justifiable selection of the independent variables, and from these curves quite unjustifiable conclusions can be drawn. The selection of the variables, therefore, is not immaterial. As composition variable, an additive property such as mass (weight- or atomic-percentage) is suitably selected. The selection of volume percentage, for example, gives complicated curves, on account of volume changes; in electrical conductivity, such a selection would represent the relation between conductivity, composition, and specific volume, instead of the relation between conductivity and composition.

Likewise, the property function ought to be so selected that it is additive for a mechanical mixture. Two principal cases are to be differentiated in the case of alloys. When the property under examination is a purely intensity magnitude, it is independent of the quantity of the phases present, and for a mechanical mixture is represented by a straight line parallel to the concentration axis. In the second case, when the property is a specific magnitude, that is, is calculated on unit quantity of the alloy, this unit must always be the same as that employed in plotting the concentration axis. For example, the specific volume is correctly represented as a function of the weight concentration, but it is incorrect to represent the density as a function of the weight percentage.

The author discusses the representation of density, specific volume, atomic volume, electrical conductivity, and the phenomena of fusion and transition.

C. S.

The Fluidity and Specific Volume of Binary Liquid Mixtures.

W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **104**, 47—52). Compare this vol., ii, 155).—Mixtures of methyl alcohol and ethyl alcohol and of methyl alcohol and propyl alcohol show a linear relationship between fluidity (expressed in *C.G.S.* units) and

specific volume. In the case of ethyl alcohol–propyl alcohol mixtures, however, the linear relationship no longer holds, and the curves for mixtures of water with methyl and ethyl alcohols both show a well-marked minimum with approximately 40% alcohol. A number of other mixtures show a. linear relationship, for example, trichloroethylene and pentachloroethane, tetrachloroethylene and carbon tetrachloride, tetrachloroethane and carbon tetrachloride, propyl acetate and amyl formate, chlorobenzene and bromobenzene at 12° and 64°, acetic acid and formic acid.   E. H. R.

Surface Deconcentration. L. BERCZELLER (*Kolloid Zeitsch.*, 1918, **23**, 31—35).—Measurements have been made of the surface tension of aqueous solutions of phenol, valeric acid, thymol, and hæmoglobin in presence of varying quantities of different alcohols, the object being to determine to what extent the depression of the concentration of the solute at the surface of the solution by the alcohol is dependent on the concentration of the latter. The surface tension measurements were made by means of a Traube stalagmometer, the drop-numbers being taken for convenience as a measure of the surface tension. As a measure of the surface deconcentration, the difference, Δ, between the drop-number of the solution containing both alcohol and solute under examination and that of a solution containing alcohol alone is taken.

The influence of the concentration of ethyl, propyl, and *iso*amyl alcohols on aqueous solutions of phenol is expressed by the equation $(\Delta \sqrt[3]{P^2}) / \sqrt{D} = \text{const.}$, where P is the concentration of the alcohol and D is proportional to the lowering of the surface tension of water by alcohol of concentration P. In the case of methyl alcohol, however, a better constant is obtained if, in the above equation, D is substituted for $\sqrt{D}$. The effect of the four alcohols on aqueous solutions of valeric acid and thymol, respectively, is satisfactorily represented by the original equation, although in the case of thymol at high concentration of alcohol the expression no longer holds. In the case of hæmoglobin, the constancy of the expression is restricted to still smaller ranges of concentration of alcohol. It is noteworthy that for each of the four solutes examined, the constants found for the alcohols, methyl, ethyl, propyl, and *iso*amyl, are always in the same proportion, approximately $5:4:3:1$. Further, when the constants found for each alcohol are divided by the factor D_0, the lowering of the surface tension of water by the solute examined, constants are obtained which are characteristic for the different alcohols and almost independent of the character of the solute.   E. H. R.

Adsorption by Hide-powder. II. VÁCLAV KUBELKA (*Kolloid Zeitsch.*, 1918, **23**, 57—68. Compare A., 1916, ii, 297).—Observations on the adsorption of hydrogen chloride from aqueous solutions by hide-powder are described. Over a period of two years, the hide-powder was found to have the same adsorption capacity. From pure aqueous solutions of hydrogen chloride, the quantity of

this which is adsorbed by the hide-powder is independent of the concentration of the solution. In presence of considerable quantities of sodium chloride, this relation no longer obtains. The adsorption in these circumstances increases with the concentration of the acid, and the form of the adsorption curve suggests that the phenomenon is of complex character. It seems probable that the first portions of acid which are removed from solution combine with the hide-powder to form a definite chemical compound. This compound appears to contain about 977 grams of hide-powder per gram-molecule of hydrogen chloride. This number agrees fairly closely with those which have been previously obtained for the molecular weight of gelatin. The further removal of hydrogen chloride from solution takes place in agreement with the usual adsorption formula. It thus appears that there are two distinct processes involved in the so-called adsorption of hydrogen chloride by hide-powder. [Compare *J. Soc. Chem. Ind.*, 665A.]

H. M. D.

The Rate of Capillary Ascension of Liquids. RICHARD LUCAS (*Kolloid Zeitsch.*, 1918, **23**, 15—22).—From Poiseuille's expression for the rate of flow of liquids in capillary tubes, the author has deduced the expression, for the rate of ascension of a liquid in a capillary tube, $h^2 = \omega/\eta \cdot r/2 \cdot \cos d \cdot t$, where h is the height to which the liquid rises in time t, ω the surface tension, η the viscosity, r the radius of the tube, and d the meniscus angle. This formula is identical in form with Ostwald's empirical formula, $h^{1/m} = kt$, if m is made $= 0\cdot5$. Experiments have been made on the rate of ascension of a number of liquids in filter-paper, the liquids used being glycerol, aniline, nitrobenzene, benzene, methyl and ethyl alcohols, ether, chloroform, carbon tetrachloride, and carbon disulphide. Three grades of filter-paper were used of widely differing porosity, and in every case the results were satisfactorily expressed by Ostwald's equation, the value of m, however, being always less than $0\cdot5$ but greater than $0\cdot4$. If k is expressed in absolute units, the equation can be written $k\eta/\omega = r/2 \cdot \cos d \cdot t =$ const. The value of this constant is independent of the liquid used and is proportional to the mean diameter of the pores of the paper. The values of this constant obtained from the different liquids for each paper agreed satisfactorily, the ratios of the porosities of the three papers used being found to be $1 : 4 : 12\cdot5$.

It is to be observed that the formula $h^2 = \omega/\eta \cdot r/2 \cos \cdot d \cdot t$, being an approximation, is only strictly true when the capillary rise is still far from completion, that is, when h is small compared with h_0, the maximum rise. The formula cannot therefore be expected to hold for glass capillaries, in which the rate of ascension is very rapid.

E. H. R.

Theory of the Osmosis and Ultra-filtration of Colloidal Solutions. WOLFGANG OSTWALD (*Kolloid Zeitsch.* 1918, **23**, 68—78).—Although the constituents of a colloidal solution appear to be separable by the expenditure of less energy than is required

for the separation of solute and solvent in the case of a molecular solution, this is entirely due to the difference in the order of magnitude of the "molar" concentration of the solutions which are compared.

The methods employed in the filtration of colloidal solutions are discussed, with particular reference to the mechanical efficiency of the filters. In comparing the behaviour of colloidal solutions in respect of ultra-filtration, it is necessary to distinguish between those portions of the dispersive medium which are associated with the disperse phase in different forms.   H. M. D.

Abnormality of Strong Electrolytes. III. The Osmotic Pressure of Salt Solutions and Equilibrium between Electrolytes. JNANENDRA CHANDRA GHOSH (T., 1918, **113,** 707—715).—By application of Clausius's virial theorem to salt solutions, it is shown that the author's theory (compare T., 1918, **113,** 449, 627) leads to the relation $i = n\{1 - \frac{1}{3}\log_e 1/a\}$, where i represents the osmotic ratio, n the number of ions resulting from a molecule of the salt, and a the activity coefficient.

By comparing the values of i for binary and ternary electrolytes which are derived from freezing-point observations with those which are calculated (1) from the above equation, and (2) from the Arrhenius equation $i = 1 + (n-1)a$, it is shown that the equation based on the Clausius theorem and the author's theory of electrolytes is in better agreement with the experimental results. The failure of the Arrhenius equation is very strongly marked in the case of ternary electrolytes.

It is shown that no change in the activity coefficient occurs when salt solutions of the same equivalent concentration are mixed together.   H. M. D.

Rhythmic Diffusion Structures in Gelatin–Salt Jellies. III. W. MOELLER (*Kolloid Zeitsch.*, 1918, **23,** 11—15. Compare this vol., ii, 301).—In connexion with his theory of jelly structure, the author has made experiments with textile fabrics which indicate how, by the displacement of superposed layers of an ultramicroscopic lattice structure, rhythmic macroscopic effects may be produced. The development of a spheritic structure when hydrochloric acid is allowed to diffuse into a semi-liquid gelatin jelly containing sodium chloride is supposed to be caused by some such displacement of the lattice structure of the gelatin accompanied by hydrolytic fission, the resulting rhythmic structure being subsequently rendered visible by deposition of colloidal particles.
    E. H. R.

Experiments in Rhythmic Banding. HARRY N. HOLMES (*J. Amer. Chem. Soc.*, 1918, **40,** 1187—1195).—Silicic acid gels have been found to exhibit well-developed rhythmic banding effects when suitable electrolytes are dissolved in the gel, which is then brought into contact with aqueous solutions which react with the

gel electrolyte to form insoluble compounds. Banded precipitates have thus been obtained of mercuric iodide, metallic gold, copper chromate, basic mercuric chloride, cuprous oxide, copper ferrocyanide, and basic lead iodide. The best results were obtained in the case of copper chromate, the bands and the intervening clear spaces being very sharply defined.

The formation of the rhythmically distributed bands is explained in terms of differences in the rate of diffusion. If the gel contains chromate ions and the aqueous solution copper ions, then the latter diffuse into the gel and a layer of copper chromate is formed at the surface of the gel. The chromate ions below this precipitation zone diffuse into the region which is now depleted of chromate ions and meet the advancing copper ions, whereby the thickness of the precipitation layer is increased. The difference in concentration of the chromate ions in contiguous layers is greatest just below the front of the thickening band, and in consequence the copper ions have to advance some distance beyond the band before the concentration of chromate ions is sufficiently large to cause precipitation of copper chromate and the formation of a new band. These conditions are repeated, with the production of precipitation zones in rhythmic distribution. H. M. D.

Isomorphous Mixtures. PAUL GAUBERT (*Compt. rend.*, 1918, **167**, 491—494).—From a general study of the properties of crystals deposited from solutions of mixtures of isomorphous salts, the author considers that the expression solid solution must be reserved for crystals, which are stable, perfectly homogeneous, and, in the case of coloured salts, almost without polychroism. Crystals formed by the regular association of very small crystals, and even in certain cases by crystalline particles themselves, must be regarded as mixed crystals. W. G.

The Retardation of the Formation of Prussian Blue in Aluminium Hydroxide Sols. H. FREUNDLICH and J. REITSTÖTTER (*Kolloid Zeitsch.*, 1908, **23**, 23—24).—Polemical in reply to Vorländer, this vol., ii, 301. E. H. R.

Effect of Dissolved Substances on the Velocity of Crystallisation of Water. III. ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1168—1184. Compare A., 1916, ii, 233, 424).—Further observations have been made on the influence of dissolved substances on the rate of crystallisation of water at a constant temperature of $-7 \cdot 0°$. From the results obtained with metallic chlorides and sulphates, alcohols and other related organic compounds, sugars and colloids, it would seem that the retarding influence of the dissolved substance is mainly determined by its degree of hydration. All the substances examined retard the crystallisation with the exception of colloidal ferric hydroxide, which at concentrations of 10—20 grams per litre produces an increase in the rate of crystallisation. The effects observed point to the conclusion that substances which form crystallo-hydrates are hydrated in solution to

a greater extent than similar substances which crystallise in the anhydrous form. In support of the view that the velocity of crystallisation depends on the degree of hydration of the solute, a distinct parallelism is found between the velocity and the heat of solution.

Experiments made with water and potassium chloride solutions in tubes of different kinds show that the velocity of crystallisation varies directly with the diameter of the bore, but is independent of the thickness of the wall of the tube.

It is supposed that the effects produced by dissolved substances are specific in nature, but it is not yet possible to calculate from these the absolute degree of hydration. H. M. D.

Effect of Dissolved Substances on the Velocity of Crystallisation of Formamide. ALBERT BRANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1184—1187).—Formamide is very susceptible to spontaneous crystallisation when but slightly undercooled, but it has been found possible to compare the influence of various alkali haloids on the velocity of crystallisation at $-2 \cdot 5^{\circ}$, which corresponds with an undercooling of $4 \cdot 75^{\circ}$. The retardation of the crystallisation is supposed to be due to solvation, the extent of which appears to run parallel with the degree of hydration in aqueous solution.

For the same degree of undercooling, the velocity of crystallisation of formamide is only about one-seventh of the velocity found for water. The difference in the rates is supposed to be connected with the greater extent to which formamide is associated. H. M. D.

The Chemical Kinetics and Constitution of Aqueous-alcoholic Solutions of Sodium Alkyloxides. RUD. WEGSCHEIDER (*Monatsh.*, 1918, **39**, 201—218).—A mathematical discussion of the kinetics of chemical changes between a solution of sodium in aqueous alcohol and substances which react with both sodium hydroxide and sodium ethoxide. The assumption of Lobry de Bruyn and Steger (A., 1899, i, 745; see also Senter and Wood, T., 1915, **107**, 1070), that the ratio between the amounts of sodium hydroxide and sodium ethoxide can be directly deduced from the relation between the quantities of the two reaction products, is erroneous, as also is therefore their conclusion that even in 50% alcohol the sodium is present mainly as sodium ethoxide. D. F. T.

Alkaline Saponification. Esterification of Citric Acids and their Glycerides. J. PINNOW (*Zeitsch. Elektrochem.*, 1918, **24**, 270—278).—The author shows that, contrary to the statement of Meyer (this vol., ii, 223), his accounts of the esterification of triethyl citrate and the hydrogen ethyl citrates constitute the first complete work on the step-wise alkaline hydrolysis of esters of a tribasic acid. The work previously published (this vol., ii, 103) is continued in the present paper. It is shown that cotton-seed

oil when treated with cold alcoholic potash is converted to the extent of 75% into the ethyl ester, whilst a small quantity is directly hydrolysed. The glycerol content in cotton-seed oil can be estimated by weighing and the use of an analytical correction. Asymmetric diethyl hydrogen citrate is hydrolysed in two ways by dilute acids. It is also shown that in preparing diethyl esters from the monoethyl esters obtained by the hydrolysis of triethyl citrate, the asymmetric diethyl ester is produced in the larger quantity. A comparison of the velocity of hydrolysis of the glycerides of acetic acid and other esters shows that the complex formation between the alkali or alcoholate does not take place with the whole ester molecule, but with dissociated groups.

J. F. S.

Atomic Structure from the Physico-chemical Standpoint.

ALFRED W. STEWART (*Phil. Mag.*, 1918, [vi], **36**, 326—336).— The question of the structure of the atom is considered more particularly with reference to the chemical properties of the elements, and a model atom is described which takes account of the following facts: (1) the independence of the α- and β-ray changes, (2) the difference in origin of the electrons which are involved in ordinary chemical changes and those which are ejected during β-ray changes, (3) the impossibility of controlling the ejection of β-ray electrons by any known process, (4) the alteration of the atomic number by either an α- or a β-ray change, (5) the production of helium in an α-ray change, (6) the difference in degree between the effects produced by the ejection of a β-ray and the corresponding change in valency produced by chemical means, (7) the possession of the same chemical properties by atoms of different weights, and, on the other hand, the identity of the weights of atoms which have different chemical properties. In this model atom, the core is negative and consists of a group of negative electrons travelling in closed orbits. Closely surrounding these are the orbits occupied by positive electrons, some of which are supposed to be associated with negative electrons. The mass of the atom is supposed to be concentrated in this zone. Further from the core, other negative electrons move in orbits of an elliptical character, the ellipses being much elongated, so that the electrons travel in paths comparable with those of comets in the solar system. When these "cometary" electrons are in a position of aphelion to the nucleus, they will be moving relatively slowly in their orbits, and hence will be less resistant to forces tending to remove them from the atom. The forces attracting the electrons towards the nucleus will also be weakest in this position, and the ease with which the valency of certain elements can be altered by chemical or electrical means can thus be readily explained. Elements which show no changes of valency may be assumed to have more nearly circular orbits for the electrons in the outer zone of the atom. For the interpretation of other properties the original must be consulted. H. M. D.

Romance of the Chemical Elements, their History and Etymology. INGO W. D. HACKH (*Amer. J. Pharm.*, 1918, **90**, 478—492, 565—579).—An account of the history and the etymology of the elements. Chronological tables and family trees of related elements serve to illustrate the historical description.

H. M. D.

Modification of the Periodic Table. INGO W. D. HACKH (*Amer. J. Sci.*, 1918, [iv], **46**, 481—501).—A more ample account of work already published (this vol., ii, 306).   C. S.

Definition of Valency. F. H. LORING (*Chem. News*, 1918, **117**, 319—322).—A general discussion of the meaning to be applied to the term valency. Valency is described as of four types: (1) that existing with helium atoms acting as subatomic units; this is a stronger type of valency, and consequently stronger affinity; (2) that involved in atomic combinations, that is, the ordinary valency, but with affinities which are not correlated to the valency values; (3) a residual or excess valency, which tends to become diffuse and is exerted in the formation of molecular complexes; and (4) a more remote type of valency, which, being wholly diffuse, is more of the nature of an affinity pure and simple, and in this case, which is active in cohesion, the idea of valency may be eliminated. The author supports his suggestions by extracts from various writers.   J. F. S.

Further Contributions to the Life-history of Johann Rudolph Glauber. WALTER BRIEGER (*Chem. Weekblad*, 1918, **15**, 984—987).—A popular account, with portrait, of the life of Glauber.   A. J. W.

Inorganic Chemistry.

Hydrogen Sulphide Generator. T. R. ERNEST (*J. Amer. Chem. Soc.*, 1918, **40**, 1224—1226).—A compact form of generator with concentric compartments for the iron sulphide and the acid. Ease of control, absence of leakage, and large storage capacity are advantageous features claimed for the author's design.

H. M. D.

Method of Handling Phosphorus. BERTRAM BLOUNT (*Analyst*, 1918, **43**, 291—292).—Phosphorus may be safely handled in a vessel filled with nitrogen free from oxygen. Carbon dioxide cannot be used for this purpose, since, should the phosphorus take fire, it will continue to burn, decomposing the gas. C. A. M.

Electrolysis of Molten Sodamide and Potassamide.
LOTHAR WÖHLER and F. STANG-LUND (*Zeitsch. Elektrochem.*, 1918,
24, 261—270).—An open apparatus is described in which pure
sodamide and potassamide may be prepared by the action of
ammonia on the molten metals. The apparatus is so constructed
that the physical constants of the product may be determined
immediately after preparation, and the purity thereby determined.
Melting points of the products were obtained from cooling curves,
and the values, sodamide, m. p. 210°, potassamide, m. p. 338°,
obtained, instead of the values 149—155° and 270—272°, re-
spectively, which had been obtained previously by Titherley (T.,
1894, **65**, 504). Apart from the breaks occasioned in the cooling
curves by the solidification of the amides, no other breaks were
observed. The method of analysis of the amides proposed by
Dennis and Browne (A., 1904, ii, 558) is modified by moistening
the amide with alcohol before its decomposition by water. This
has the effect of making the decomposition occur more regularly.
The molten amides conduct a current electrolytically, due to the
ionisation $NaNH_2 \rightleftharpoons Na^{\cdot} + NH'_2$. Hydrazine is not formed at
the anode as was expected, but ammonia and nitrogen, the dis-
charge of the anion taking place according to the equation
$6NH_2' + 6\oplus = 4NH_3 + N_2$. The expected formation of hydrazine
was probably prevented by the catalytic action of the sodamide.
Chlorine and iodine do not form hydrazine with the amides, but
halogen-substituted ammonias. The specific conductivity has been
determined, and the values $x_{210°} = 0.593$ ohm^{-1} for sodamide and
$x_{340°} = 0.389$ ohm^{-1} for potassamide, obtained. The decomposition
voltage at the melting point is found to be 0.71 volt for sodamide
and 0.87 volt for potassamide, the former having a temperature
coefficient 1.52×10^{-3} volt. J. F. S.

**Alteration in Concentrated Solutions of Sodium Hypo-
chlorite.** M. BOUVET (*Bull. Sci. Pharmacol.*, 1917, **24**, 347—349;
from *Chem. Zentr.*, 1918, i, 941).—Concentrated solutions of
sodium hypochlorite rapidly lose their activity in direct sunlight.
Decomposition occurs most readily in white glass flasks, consider-
ably more slowly in vessels of brown glass. Solutions preserved
in the shadow or in the dark are practically unchanged after four
weeks. H. W.

**Microchemical Reactions of Metals with Rubidium and
Cæsium Chlorides.** JAN VERMANDE (*Pharm. Weekblad.*, 1918,
55, 1131—1134).—An account of the preparation of double
chlorides of cæsium and rubidium with mercury, silver, copper,
bismuth, antimony, tin, lead, nickel, cobalt, cadmium, iron, zinc,
manganese, and magnesium. These chlorides are analogous to the
corresponding double salts of potassium and sodium. No double
chlorides were obtained containing arsenic, aluminium, calcium,
strontium, barium, potassium, sodium, or lithium. A. J. W.

Silver Arsenide. I. Attempt to Reduce Silver Arsenate by Formaldehyde. ENRIQUE V. ZAPPI and JUAN L. LANDABURU (*Bull. Soc. chim.*, 1918, [iv], **23**, 318—322).—Attempts to reduce silver arsenate either in the solid state or in hot or cold ammoniacal solution with formaldehyde were not successful. The product from the latter method oscillated in composition around that expressed by the formula $2Ag_3AsO_4,Ag$.   W. G.

Thermal Decomposition of certain Inorganic Trinitrides. ARTHUR R. HITCH (*J. Amer. Chem. Soc.*, 1918, **40**, 1195—1204). —The possibility of regulating the decomposition of metallic trinitrides, when heated, has been examined in experiments conducted at different temperatures. Silver, mercurous, mercuric, barium, and thallous trinitrides decompose quickly into the corresponding elements when the temperature is suitably adjusted, but the behaviour of lead, cupric, and ammonium trinitrides is not so easily controlled. In the case of silver trinitride, which was more closely examined, quiet decomposition occurs at 280—290°. The rate of decomposition was found to increase with the temperature, and in a vacuum the evolution of nitrogen was much more rapid than at atmospheric pressure.

An arrangement of apparatus is described in which the thermal decomposition of the trinitrides may be quantitatively determined, and it is proposed to make use of this in the determination of the atomic weight of nitrogen.   H. M. D.

An Impurity of Zinc Dust. O. BINDER (*Chem. Zeit.*, 1918, **42**, 458).—Zinc dust frequently contains a considerable amount of chlorine, and should be proved free therefrom before being used for reductions in analytical work.   C. A. M.

Basic Carbonate of Copper. HORACE BARRATT DUNNICLIFF and SUDARSHAN LAL (T., 1918, **113**, 718—722).—The statement that commercial copper carbonate has the same composition as malachite is not in agreement with the authors' results for thirteen samples which have been examined. Attempts to prepare a basic copper carbonate of approximately constant composition have shown that a substance of the composition $2CuCO_3,5Cu(OH)_2$ may be obtained by the action of a mixture of sodium carbonate and sodium hydrogen carbonate on copper sulphate solutions.   H. M. D.

The Rare Earths. VII. Separation of Holmium. L. F. YNTEMA and B. S. HOPKINS (*J. Amer. Chem. Soc.*, 1918, **40**, 1163—1167).—Experiments made with rare earth fractions containing only holmium and yttrium indicate that these may be separated by fractional hydrolysis of the phthalates. By gradually raising the temperature of the phthalate solution, basic phthalates are precipitated, and the first fractions are found to contain a larger proportion of holmium than that present in the original rare earth mixture.

Fractional precipitation by sodium nitrate from a dilute neutral nitrate solution also leads to an accumulation of holmium in the first fractions. A holmium–yttrium mixture with an "atomic weight" equal to 97·7, when separated into six fractions by this method, gave 103·3 for the "atomic weight" of the metal in the first fraction and 91·3 in the last fraction. The nitrite method is considered to promise better results than the phthalate method.

<div align="right">H. M. D.</div>

Fusion and Crystallisation of Iron–Carbon Alloys. RUDOLF RUER and FRANZ GOERENS (*Ferrum.*, 1917, **14**, 161—177; from *Chem. Zentr.*, 1918, i, 907. Compare Ruer and Iljin, A., 1911, ii, 494; Ruer and Goerens, A., 1916, ii, 483; 1917, ii, 474). —With the object of reinvestigating certain portions of the equilibrium diagram of iron–carbon alloys, the authors have melted pure electrolytic iron with sugar carbon in an electric furnace in porcelain tubes in an atmosphere of nitrogen. The melting points of antimony (630·6°), copper (1084°), and nickel (1451°) were used for the calibration of the thermometer. The mean of the melting and solidifying points of the cementite eutectic is found to be 1145°, that of the graphite eutectic 1152°; the former alloy contains 4·2% and the latter 4·15% of carbon. The perlite point occurs at 721° with 0·9% of carbon. The authors draw the conclusion that the formation of graphite in grey pig iron occurs in the liquid phase, and that the substance separates as such from the molten mass and is not formed by the disintegration of other pre-formed crystalline varieties.

A résumé of the data which are necessary for the construction of the melting-point curves is appended.

<div align="right">H. W.</div>

High Temperature Investigations. XI. Chromium and Carbon. OTTO RUFF and THEODOR FOEHR (*Zeitsch. anorg. Chem.*, 1918, **104**, 27—46).—An account of a detailed study of the alloys of chromium and carbon. Alloys saturated with carbon were prepared by melting chromium (prepared by the alumino-thermite process and containing Al 1·33%, Fe 0·62%, Si 0·26%, Al_2O_3 0·53%) in a crucible of pure carbon at temperatures varying from 1840° to 2567° for fifteen minutes, stirring frequently with a carbon rod. Samples less rich in carbon were obtained by melting a mixture of chromium and a finely powdered alloy containing 11·16% of carbon in a magnesia crucible at 1800—1850°. At higher temperatures, chromium attacks the crucible. Alumina or zirconia is no more resistant than magnesia. For the analysis of the alloys, special methods were devised, consisting in oxidising by means of potassium nitrate or sodium peroxide, carbon and chromium being converted, respectively, into carbonate and chromate.

The alloys of carbon and chromium fall into two groups: (1) those containing up to 8·5% of carbon, completely soluble in hot 24% hydrochloric acid; (2) those containing more than 8·5% of carbon, partly soluble in the same acid.

The alloys of the first group, which have been prepared containing 1·51% to 8·49% of carbon, when repeatedly extracted with cold 2N-hydrochloric acid until no more chromium dissolves, leave a residue of practically pure Cr_5C_2. The low carbon alloys show a close fracture, those with a higher carbon content being coarser and showing distinct crystalline needles. Microscopic sections etched with hydrochloric acid (no other etching reagent is applicable to these alloys) show crystals of the compound embedded in a eutectic. The alloy containing 8·49% of carbon is practically pure Cr_5C_2 and contains no eutectic, the section showing a uniform mass of crystals. The carbide, Cr_5C_2, which can be prepared in quantity, forms silvery crystals, $D_4^{24\cdot8}$ 6·915, m. p. 1665°. It is not attacked by aqua regia, and on melting undergoes no appreciable decomposition. No trace of the compound Cr_4C described by Moissan was found.

The alloys of the second group, containing more than 8·5% of carbon, contain no free chromium, only carbide and graphite. The carbon content of the saturated alloys increases with the temperature of preparation, from 12·42% at 1840° to 14·03% at 2233°, and more rapidly to 23·12% at 2567°. When treated with hot 24% hydrochloric acid, part of the alloy dissolves, the ratio of chromium to carbon dissolved indicating that the soluble carbide has the composition Cr_4C_2. The existence of this compound could not be confirmed by isolation. The residue insoluble in hot acid contains graphite, together with the carbide, Cr_3C_2, which, after extraction of the graphite, is obtained 99—99·5% pure. The three constituents, Cr_3C_2, Cr_4C_2, and graphite, can be identified in microscopic sections, which show no eutectic. Possibly above 2250° a higher carbide, CrC, is formed.

The carbide, Cr_3C_2, is resistant to all acids. It is darker in appearance than Cr_5C_2, has $D_4^{21\cdot3} = 6\cdot683$, and melts at about 1890 ± 10°. In the molten condition, it reduces magnesia, alumina, and zirconia, and apparently undergoes partial decomposition when melted into Cr_4C_2 and graphite. It is decomposed by chlorine at a red heat, forming chromium trichloride and amorphous carbon.

The chemical composition of the alloys rich in carbon is unaffected by the rate of cooling, but larger crystals are developed when the rate of cooling is retarded. An alloy saturated with carbon boils at about 2570° under 8—14 mm. pressure, the vapour being pure chromium.

From the data obtained, the equilibrium diagram for the system chromium–carbon has been constructed.   E. H. R.

Metastannic Acid and its Compounds. AUGUST KLEINSCHMIDT (*Monatsh.*, 1918, **39**, 149—178).—On account of the discrepancies in the literature concerning the action of nitric acid on tin, a reinvestigation has been made. If nitric acid is diluted with 1¼—2 volumes of water, the only product is stannous nitrate, and with stronger, and even undiluted, acid at 0—15°, the formation of stannous nitrate can still be observed, accompanied by

normal or basic stannic nitrate; within the stated range of tempera-
ture, the yellowish-white precipitate which may be formed consists
of a mixture of white stannic nitrate soluble in water with in-
soluble, yellowish-white basic stannic nitrate. Stannic nitrate
even at the ordinary temperature slowly changes into the meta-
salt, and for this reason the white, bulky precipitate which it
yields with aqueous sodium hydroxide may not dissolve completely
in an excess of the reagent; at 45°, the change in the stannic
nitrate is so rapid that the solution suddenly gelatinises, and, after
prolonged heating at 100°, the transformation is complete. The
powdery product of oxidation of tin with hot nitric acid, commonly
described as metastannic acid, is really a nitrate of metastannic
acid which, on washing with water, gives rise to metastannic acid
as a secondary hydrolytic product. Metastannic acid, obtained by
the action of nitric acid (D 1·40) on tin and careful washing with
water, when dried in air at the ordinary temperature has the com-
position $5H_2SnO_3,4H_2O$, the $4H_2O$ being lost on storage over
sulphuric acid in a vacuum for several days; the nitric acid is
removed only with difficulty, and if alcohol is used instead of
water, the washing has to be still more prolonged; the primary
oxidation product is therefore in all probability a metastannic
nitrate which yields metastannic acid by hydrolysis. Metastannic
acid shows no double refraction under the polarisation microscope
and is an amorphous powder; it is capable of combining with
hydrochloric acid or sulphuric acid with development of heat, the
resulting compounds being very easily hydrolysable. The quinque-
molecular formula for the anhydrous acid is confirmed by an
analysis of sodium metastannate, produced by the action of sodium
hydroxide on metastannyl chloride, the resulting compound having
the composition $5SnO_2,Na_2O,4H_2O$. The parastannic acid described
by Engel (A., 1898, ii, 29) is ordinary metastannic acid. Meta-
stannic nitrate, prepared by the action of hot nitric acid on tin,
has the composition $5SnO_2,2HNO_3,3H_2O$, whether dried in a
vacuum over sodium hydroxide and calcium chloride or between
porous tiles in the air; the compound obtained from tin and cold
nitric acid probably consists of a mixture or compound of stannyl
nitrate, $SnO(NO_3)_2$, and the above metastannic nitrate; both
nitrates gradually decompose in ultra-violet light with liberation
of nitric acid. The action of hydrochloric acid on metastannic
acid yields a stannyl chloride which, after being washed free from
soluble tin salts by diluted hydrochloric acid and dried in a vacuum
over sodium hydroxide and calcium chloride, has the composition
$5SnO_2,2HCl,3H_2O$; the primary, pasty product, on account of its
content of free acid, gives a clear solution in water, but when dry
does not dissolve entirely on account of hydrolysis. As simple
α-stannic acid and the β-metastannic acid are colloidal substances
capable of reversible inter-transformation, the change occurring
more readily, however, from the α-acid to the meta-acid, these facts
accord well with the respective formulæ H_2SnO_3 and $(H_2SnO_3)_5$;
the structure of the latter is represented by a cyclic skeleton con-

taining five tin atoms and five oxygen atoms, arranged alternately with ten hydroxyl groups attached in pairs at each tin atom. The stannyl chloride is therefore represented as $Sn_5O_5(OH)_8Cl_2$, the metanitrate as $Sn_5O_5(OH)_8(NO_3)_2$ and the metasulphate as $Sn_5O_5(OH)_8SO_4$.   D. F. T.

Presence of Vanadium and Arsenic in the Subterranean Waters of Bell-ville (Cordova). ATILIO A. BADO (*Bol. Acad. Nac. Ciencias, Cordoba*, 1918, **23**, 85—96).—An account of analyses of water from the district of Bell-ville, in Argentina.

A. J. W.

Mineralogical Chemistry.

Hydrothermal Mineral Formation. WOLF J. MÜLLER and
J. KOENIGSBERGER (*Zeitsch. anorg. Chem.*, 1918, **104**, 1—26).--
The investigations described in an earlier communication have
been continued (A., 1906, ii, 553). The experiments have been
confined to the system $K_2O–Al_2O_3–SiO_2–H_2O$, with or without
carbon dioxide. The starting materials used were potassium
silicate (potassium water glass) and an aluminium hydroxide
hydrogel, or in some cases a 0·5 molar solution of potassium
aluminate. Carbon dioxide was added either as potassium
carbonate or as solid pellets just before closing the bomb. The
several constituents in the proportions required were heated for
varying lengths of time (12 to 180 hours) at temperatures varying
from 100° to 440° in a strongly made bomb. Inside the bomb was
a filter tube, so arranged that by inverting the furnace the liquid
contained in the bomb could be filtered into this tube, and any
crystals separating subsequently collected and examined. The
products were identified generally by optical methods.

On few occasions were any crystals obtained in the filter tube,
the only products identified being quartz, orthoclase, zeolite, and
pectolite, not leucite or nepheline. With rising temperature, the
quantity of leucite in the solid phase diminishes, that of orthoclase
increasing. From the slight amount of filter-tube product
obtained, it is clear that the concentration of potassium aluminium
silicate in the water at the temperatures employed is low, and is
not likely appreciably to affect the critical temperature of the
water.

Potassium felspar was only identified when the temperature
used was 360° or above. This critical temperature (360±20°)
should be an important fixed point for the geological thermometer.
The presence of carbon dioxide or of sodium or calcium ions intro-
duced in the form of labradorite does not affect the critical tempera-
ture. Albite was not observed up to 430°, but Baur has obtained

it under similar conditions at 450° (A., 1911, ii, 991). In presence of carbon dioxide at 310°, quartz alone is stable, the alumino-silicates appearing to be transitional with short heating at lower temperatures, forming again with longer heating at higher temperatures. The succession of minerals observed in nature is in better agreement with the results of experiments in which much carbon dioxide was present than in those without.

The formation of zeolites in absence of carbon dioxide commences below 100° and may increase up to 400°, but probably their limit of stability, with the exception of analcime, is below 300°.

The opinion is confirmed that, in hydrothermal syntheses below 400°, equilibrium is seldom attained. E. H. R.

Meteoric Iron from Chili (Dehesa). F. BERWERTH (*Tsch. Min. Mitt.*, 1917, **34**, 272).—This mass was described by Daubrée in 1868, and was stated by Domeyko to have been found in the Cordillera de la Dehesa, near Santiago. From its compact appearance and Domeyko's analysis (Ni 14%), it was placed in the group of nickel-rich 'compact irons.' Microscopical examination of an etched surface shows, however, that the structure is octahedral. The following new analysis (mean of two by E. DITTLER) was therefore made, showing that this iron belongs to the group of very fine octahedrites.

Fe.	Ni.	Co.	Insol. (Schreibersite).
87·40	11·97	0·56	0·07

L. J. S.

Analytical Chemistry.

Calculation of the Possible Error in Gravimetric Estimations. V. ZOTIER (*Bull. Sci. Pharmacol.*, 1917, **24**, 298—302 ; from *Chem. Zentr.*, 1918, i, 945).—In the gravimetric estimation of the amount, x, of a substance, X, dissolved in water by conversion into an insoluble substance, Y, and weighing the quantity of the latter, y, the possible total error, exclusive of that due to the personal factor, is exactly equal to the algebraic sum of the individual errors. If m_1 and m_2 are the molecular weights of X and Y, respectively, Δm_1 and Δm_2 the accuracy of their determination (the value $O = 16$ being considered exact as fundamental), the relative error is expressed by the following relationship :

$$\Delta x / x = (m_2 y . \Delta m_1 + m_1 y . \Delta m_2 + m_1 . m_2 \Delta y) / (x . m^2{}_2).$$

The estimation of sulphuric acid by weighing the barium sulphate formed is chosen as example ; the possible sources of error are the solubility of the sulphate in water, adhesion of the precipitate to the glass, adhesion of foreign matter to the precipitate,

the weight of dust falling on the precipitate during the estimation, increase in weight of the crucible by deposition of moisture, errors in weighing, and loss during incineration. Of these, the solubility and the error in weighing can be mathematically treated; the others are, in part, independent of y, and their sign and magnitude can only be arbitrarily estimated. In the case given above, the uncertainty is calculated to be 11:1000.   H. W.

Colorimetric Determination of the Reaction of Bacteriological Media and other Liquids. G. D. BARNETT and H. S. CHAPMAN (*Amer. J. Pharm.*, 1918, **90**, 592—595).—The method depends on the superimposing of two extreme colours of the indicator, as first proposed by Salm (A., 1906, ii, 218). For example, in the case of a phenolsulphonephthalein solution, the observed colour may be regarded as being composed of a definite amount of red with a definite amount of yellow, and may be matched by superimposing the extreme red and extreme yellow of the indicator in proper concentrations. If five drops of a solution of this indicator be added to a tube containing 5 c.c. of dilute acid, and five drops to another tube containing 5 c.c. of dilute alkali, the colour observed by transmitted light through both tubes will be half-way between the yellow and the red. This is the half-transformation point, and is a definite constant for this indicator. By partitioning the ten drops of indicator in varying proportions between tubes containing the same amounts of acid and alkali, and viewing each pair by transmitted light, a series of colours covering the range of usefulness of this indicator ($6·9$ to $8·1$ p_H) will be obtained. By standardising the series by comparison with solutions of known hydrogen-ion concentration, it may be used as a colour standard for the determination of unknown reactions.

C. A. M.

Simple Application of the Volhard Principle for the Estimation of Chlorides in Blood Plasma. W. C. RAPPLEYE (*J. Biol. Chem.*, 1918, **35**, 509—512).—The citrated plasma is diluted with water, the chlorides precipitated by a standard solution of silver nitrate, and, after filtration, the excess of silver titrated by potassium thiocyanate, using iron ammonium alum as an indicator. Employing a silver nitrate solution of such a strength that 1 c.c. is equivalent to $2·5$ mg. of sodium chloride, and a thiocyanate solution of one-fifth of the strength of the silver nitrate solution, the error in the estimation of the chlorides in 2 c.c. of the plasma does not exceed 1%.   H. W. B.

Important Alteration in a Sodium Thiosulphate Solution. H. I. WATERMAN (*Chem. Weekblad*, 1918, **15**. 1098—1099).— From May to August, the strength of a sodium thiosulphate solution, as determined by the iodine method, altered from $0·923 \times N/10$ to $1·021 \times N/10$. The author is unable to suggest an explanation of the phenomenon.   A. J. W.

Simplified Gasometric Estimations. ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [vii], **18**, 104—106).—To avoid frequent standardisations of the nitrometer in the estimation of nitrogen in urea, a second tube, exactly similar to the nitrometer tube, is employed. A known amount of urea is decomposed as usual in the nitrometer, and the volume of nitrogen obtained is noted. The same volume of air is then admitted to the comparison tube, and this volume is used as the standard in subsequent estimations. [See, further, *J. Soc. Chem. Ind.*, November.] W. P. S.

A Survey of Methods for the Estimation of Nitrites and Nitrates in the same Solution. ALICE OELSNER (*Zeitsch. angew. Chem.*, 1918, **31**, 170—172, 178—179).—The various methods available for the estimation of nitrites and nitrates in presence of each other are reviewed. The colorimetric methods are suitable for water analysis. The diphenylamine–sulphuric acid reagent is available for both nitrates and nitrites, since, when diluted with a definite volume of water, it ceases to react with nitrates and shows a blue colour with nitrites. The nitrites are estimated first and then destroyed with urea and sulphuric acid or by boiling with ammonium chloride; this treatment does not affect the nitrates. Letts and Rea (T., 1914, **105**, 1157) recommend diphenylbenzidine. Several gasometric methods have been described, depending on the evolution and measurement of nitrogen or nitric oxide. For instance, on boiling a nitrite with ammonium chloride, nitrogen is evolved equivalent to twice that of the nitrite; the presence of nitrate has no influence. Ferrous chloride in presence of acetic acid or ferrous ammonium sulphate alone, on boiling, decompose nitrites with evolution of nitric oxide, which may be measured in a eudiometer. The subsequent addition of hydrochloric acid to the same solution causes the decomposition of the nitrates according to Schlœsing's method. Nitric oxide may also be liberated first by hydriodic acid, which decomposes nitrites, and then by ferrous chloride and hydrochloric acid, which decomposes nitrates. Winogradsky prefers to estimate the nitrites by titration with permanganate, with the formation of nitrate, and then the total nitrates by Schlœsing's method. In the analysis of culture media for the study of the progress of nitrification and denitrification by bacteria, the author recommends the permanganate method, the solution of nitrite being titrated into the diluted permanganate, previously acidified and warmed to 40°. Towards the end of the titration, plenty of time must be allowed between each addition, as the oxidation is somewhat slow. The total nitrogen is then determined as ammonia after reduction by zinc and iron in alkaline solution. The method gives much closer results than Winogradsky's, and is applicable to culture liquids which do not contain ferrous sulphate, which, moreover, is not essential for the growth of these bacteria.

The culture media may contain small quantities of other reducing substances which involve a constant error, generally negligible.

Citric acid is generally employed, but does not affect the nitrite titration performed in the manner described. Ammonium salts are eliminated by boiling before reduction of the total nitrate. Franzen and Löhman (A., 1909, ii, 517) have criticised the gasometric methods as applied to bacteriological work, and recommend Busch's method (A., 1906, ii, 392) for liquids containing much organic matter, based on oxidation of nitrites by peroxide and their decomposition by hydrazine sulphate, the nitrates being determined in both portions by precipitation with nitron. Methods of minor importance have been based on the precipitation of nitrites by 2 : 4-diamino-6-hydroxypyrimidine sulphate, and on the elimination of nitrites by esterification with methyl alcohol in presence of standard hydrochloric acid, the loss of acidity being determined.   J. F. B.

Gravimetric Estimation of Phosphates. W. R. MUMMERY (*Analyst*, 1918, **43**, 324).—Complete precipitation of phosphoric acid may be effected by a modification of Ullmann's method, in which the nitric acid solution is filtered prior to dilution to a standard volume. Phosphomolybdates are precipitated at 60° and allowed to remain for thirty minutes at 60°, whilst magnesium ammonium phosphate is precipitated at 80° and left for three hours at the ordinary temperature.   C. A. M.

The Estimation of Phosphoric Acid as Magnesium Pyrophosphate. IV. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1918, **104**, 53—56).—On account of the slight solubility of the two phosphates $Mg[(NH_4)_2PO_4]_2$ and $Mg_3(PO_4)_2$, it is practically impossible to get true equilibrium in solution and is difficult to obtain a pure precipitate of normal magnesium ammonium phosphate (compare this vol., ii, 332). When the velocity of precipitation is retarded by allowing ammonia to diffuse slowly into an acid solution of the phosphoric acid–magnesia mixture in presence of ammonium chloride in the cold, the precipitate is practically pure $MgNH_4PO_4$. Experiments on the method of Schmitz, by which ammonia is added to a hot solution in presence of ammonium chloride and precipitation occurs on cooling, show that the precipitate thus produced is not pure. On ignition, part of the phosphoric acid is lost by volatilisation, and the residue is relatively rich in magnesium and poor in phosphoric acid, the errors approximately compensating one another. It is therefore inadvisable to redissolve and reprecipitate after ignition. The result obtained by this method is not affected by variations in dilution or in the quantity of ammonium chloride present.   E. H. R.

Rapid Micro-method for the Estimation of Phosphate and Total Phosphorus in Urine and Stools. AKIRA SATO (*J. Biol. Chem.*, 1918, **35**, 473—477).—The phosphate is precipitated by uranium in the presence of sodium acetate and acetic acid, alcohol being added to facilitate precipitation and filtration.

The uranium phosphate is then dissolved in acid and the solution treated with potassium ferrocyanide. A red colour is developed, the intensity of which is compared in a colorimeter with that produced in a similar manner from a standard uranium phosphate solution in hydrochloric acid. H. W. B.

Use of Manna in the Estimation of Boric Acid. LILLIAN E. ILES (*Analyst*, 1918, **43**, 323).—A freshly prepared solution of manna can replace glycerol in the estimation of boric acid. As a rule, about 5 grams of manna in solution are equivalent to about 25 c.c. of 80% glycerol. C. A. M.

Estimation of Silicon in Ferrosilicon. P. NICOLARDOT and J. KOENIG (*Ann. Chim. anal.*, 1918, **23**, 169—173).—The ferrosilicon is fused with sodium carbonate and potassium nitrate, and the silica then estimated by the usual methods. W. P. S.

Estimation of Total Carbon in Various Biological Substances. ANDRÉ RENAUD (*J. Pharm. Chim.*, 1918, [viii], **18**, 106—108).—The substance is heated with sulphuric acid and potassium dichromate, and the resulting carbon dioxide, together with other gases, is absorbed in ammoniacal calcium chloride solution. The resulting calcium carbonate is then estimated volumetrically. If ammoniacal barium carbonate is used for the absorption, the barium carbonate obtained may be converted into barium sulphate and weighed as such. [See, further, *J. Soc. Chem. Ind.*, November.] . W. P. S.

Estimation of Potassium. THOS. STEEL (*Analyst*, 1918, **43**, 348—349).—The hydrochloric acid solution containing the potassium, and also iron, calcium, magnesium, etc., but free from silica, is evaporated with the addition of an excess of platinum chloride, and the residue obtained is treated with a mixture of alcohol, 76, ether, 13, water, 11 parts. The precipitate is collected, washed with the alcohol–ether–water mixture, then dissolved in boiling water, and the solution boiled with an excess of sodium formate; after a few minutes, hydrochloric acid is added, the heating continued until the reduced platinum has flocculated, and the platinum then collected, washed, ignited, and weighed. W. P. S.

Volumetric Estimation of Barium and the Solubility of Barium Chromate in Various Aqueous Solutions. JOHN WADDELL (*Analyst*, 1918, **43**, 287—289).—Barium chromate, as obtained in the separation of strontium and calcium, may be determined by a method analogous to that used for lead.

The precipitate of barium chromate (about 0·15 gram) is collected on asbestos in a Gooch's crucible and dissolved in 25 c.c. of strong hydrochloric acid and 75 c.c. of water, and the solution made up to 200 c.c. About 6 grams of potassium iodide are

added, and, after ten minutes, the liberated iodine is titrated with standard thiosulphate solution. It is essential that the hydrochloric acid should be cold and dilute to prevent liberation of chlorine by the chromate. The method has been used to determine the solubility of barium chromate in water and various aqueous solutions under the ordinary conditions of washing a precipitate. The results showed that for washing barium chromate, pure water is preferable to 1% ammonium acetate solution, which dissolves about four times as much of the salt as water.   C. A. M.

Method for the Separation and Estimation of Barium Associated with Strontium. F. A. GOOCH and M. A. SODERMAN (*Amer. J. Sci.*, 1918, **46**, 538—540).—Barium and strontium may be separated by treating the saturated solution of their chlorides with a mixture of concentrated hydrochloric acid and ether (4:1); about 50 c.c. of this mixture are required for 0·5 gram of the mixed salts. The precipitated barium chloride is then collected on an asbestos filter, washed with the hydrochloric acid–ether mixture, dried at 150°, and weighed. [See, further, *J. Soc. Chem Ind.*, November.]   W. P. S.

Volumetric Estimation of Zinc. R. HOWDEN (*Chem. News*, 1918, **117**, 322).—Zinc can be estimated volumetrically as chloride and in the absence of salts of ammonium and the heavy metals in the following way. The solution is evaporated to remove most of the free acid and then exactly neutralised by $N/10$-sodium hydroxide, using one drop of methyl-orange as indicator. The solution is then titrated further with $N/10$-sodium hydroxide, using phenolphthalein as indicator. Towards the end of the titration, the solution is boiled, and the end-point taken as that point where the pink colour remains on boiling. The method is stated to give absolutely concordant results.   J. F. S.

Analysis of Commercial Zinc. L. BERTIAUX (*Ann. Chim. anal.*, 1918, **23**, 161—169, 181—191).—Methods are described in detail for the estimation of the following impurities in commercial zinc: lead, iron, cadmium, sulphur, carbon, copper, arsenic, and antimony. Analyses of forty-two samples are recorded. The maximum amount of copper found was 0·012%, of tin 0·576%, of iron 0·210%, of lead 2·327%, of cadmium 0·380%, of sulphur, trace, and of carbon 0·033%. Arsenic and antimony were present in traces only. [See, further, *J. Soc. Chem. Ind.*, 658A.]   W. P. S.

Separation of Traces of Copper from Solution. J. E. SAUL and DAVID CRAWFORD (*Analyst*, 1918, **43**, 348).—The antiseptic known as quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives a precipitate with traces of copper. If 0·1 gram of quinosol is dissolved in 100 c.c. of water containing 0·0002 gram of copper (as a salt), a voluminous, yellow precipitate

forms within eighteen hours; the precipitate is soluble in dilute hydrochloric acid. By means of this reagent, copper may be detected in distilled water which has been stored in copper vessels. Other metals in very dilute solution do not give a reaction, but a precipitate may be obtained from a concentrated solution of a mercuric salt. W. P. S.

The Detection of Mercury in Urine, with Employment of a New Solvent for Mercuric Sulphide. S. GUTMAN (*Biochem. Zeitsch.*, 1918, **89**, 199—203).—The solvent in question is a solution of hydriodic acid, prepared by dissolving 5 grams of potassium iodide in 12 c.c. of 10% sulphuric acid, and diluting to 25 c.c. The urine is treated first with hydrochloric acid and potassium chlorate to destroy the organic matter. From the slightly acid solution, mercury is precipitated by hydrogen sulphide. The sulphide is purified by dissolving in aqua regia and reprecipitation with hydrogen sulphide. This precipitate, if it is mercuric sulphide, should be insoluble in hot nitric acid solution, but soluble in aqua regia and the given solution of hydriodic acid. S. B. S.

Adsorption of Colloidal Hydroxides. K. SCHERINGA (*Pharm. Weekblad*, 1918, **55**, 1070—1074).—The author considers that in analysis the adsorption of ordinary salts by metallic hydroxides has not much practical significance. In separating iron, a large excess of alkali is undesirable. A. J. W.

Precipitation of Iron by Hydrogen Sulphide. R. WINDERLICH (*Zeitsch. physikal. Chem. Unterr.*, 1917, **30**, 254; from *Chem. Zentr.*, 1918, i, 814).—It is commonly stated that hydrogen sulphide does not produce a precipitate in solutions of ferrous salts. This is so only in solutions in mineral acids. Even Gay-Lussac mentioned that in the presence of sodium acetate a precipitate of ferrous sulphide is obtained. Ferrous sulphide is also precipitated from solutions of ferrous acetate in acetic acid and of iron powder in citric or succinic acid. C. S.

Use of Titanium Trichloride as a Reducing Agent in the Estimation of Iron by Titration with Permanganate in Hydrochloric Acid Solution. L. BRANDT (*Chem. Zeit.*, 1918, **42**, 433—434, 450—451).—Titanium trichloride solution may be used in place of stannous chloride solution for the reduction of ferric salts previous to the titration of the latter with permanganate solution. The ferric salt may be reduced by the addition of exactly the requisite quantity of the titanium trichloride solution, or an excess may be added, and this excess then removed by means of copper sulphate. The presence of platinum chloride, potassium dichromate, or arsenic acid in the ferric salt solution does not affect the results. Copper sulphate may also be used for removing excess of stannous chloride when this is employed for reducing the ferric salt. W. P. S.

The Colorimetric Estimation of Cobalt. E. GABRIEL JONES (*Analyst*, 1918, **43**, 317—319).—Small quantities of cobalt (0·01 to 0·1%) may be colorimetrically estimated by means of a solution of α-nitroso-β-naphthol, as used by Atack (A., 1915, ii, 652), ammonium citrate solution being added to eliminate the effect of moderate quantities of many other metals. In the case of varnishes, a solution of the ash from the sample in hydrochloric acid is treated with the reagents, and the coloration compared with those given by different quantities of a standard solution of cobalt containing the same amounts of ammonium citrate and α-nitroso-β-naphthol. About 0·1 mg. of cobalt is the most satisfactory quantity for the comparison. It is essential that the solutions should contain about the same amount of free ammonia. Iron, zinc, and lead do not interfere with the estimation, but copper, nickel, or manganese, if present in notable quantities, must be removed prior to the estimation.   C. A. M.

Estimation of Tin in High-grade Wolfram Ores, and the Use of Lead as a Reduction Agent in Pearce's Assay. A. R. POWELL (*J. Soc. Chem. Ind.*, 1918, **37**, 285—287T).—One gram of the finely ground sample is added to 5 grams of fused "bisulphate," the mixture heated to redness, then cooled, and boiled with about 80 c.c. of 5% tartaric acid solution. The insoluble portion is collected, washed with hot water, ignited while wet in an iron crucible and fused with sodium peroxide, and the tin estimated in the usual way. Traces of tin remaining in the tartaric acid solution may be recovered by means of hydrogen sulphide. The results obtained are trustworthy and agree with those found by the aqua regia method, the potassium cyanide fusion method, and the sodium peroxide fusion method. Lead may be used for the reduction of stannic salts. The solution from the sodium peroxide fusion is rendered slightly acid with hydrochloric acid, diluted to 100 c.c., 20 grams of sodium chloride, 40 c.c. of concentrated hydrochloric acid and 10 grams of granulated lead are added, and the solution is boiled for twenty minutes after the disappearance of the ferric chloride colour. A piece of marble is then added, the solution cooled, diluted with 50 c.c. of dilute sodium hydrogen carbonate solution, and titrated with iodine solution without removing the excess of lead.   W. P. S.

Quantitative Estimation of Vapours in Gases. A Differential Pressure Method. HAROLD S. DAVIS and MARY DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, **10**, 709—712).—The method depends on the fact that the vapour pressure from a liquid is independent of the kind of gas above it, provided the gas is inert (Dalton's law of partial pressure); deviations from this law are known, but it holds in the case of benzene and air. If two flasks are connected by a manometer, one of the flasks containing air and the other a mixture of air and benzene vapour corresponding with a pressure less than the saturation pressure,

and a small bulb of benzene is broken in each flask, the liquid benzene in the second flask will add only the amount of pressure necessary to bring its pressure up to saturation; the benzene in the flask containing air only will, however, produce the total saturation pressure, and the manometer will register a difference in pressure equal to the pressure of the vapour in the original gas mixture. W. P. S.

Application of the Differential Pressure Method to the Estimation of Benzene and the Total Light Oil Content of Gases. HAROLD S. DAVIS, MARY DAVIDSON DAVIS, and DONALD G. MACGREGOR (*J. Ind. Eng. Chem.*, 1918, **10**, 712—718). —Details of procedure are given for the application of this method (preceding abstract) to the estimation of benzene, toluene, and xylene in gases. W. P. S.

Absorption of Light Oils from Gases. HAROLD S. DAVIS and MARY DAVIDSON DAVIS (*J. Ind. Eng. Chem.*, 1918, **10**, 718—725).—The vapour pressure of benzene from its solution in oil is governed by Henry's law for the solubility of gases in liquids and by Babo's law for the constancy of the fractional lowering of the vapour pressure from a solution over variations in temperature, and the flow of oil necessary to remove completely the benzene from a gas may be calculated accordingly. Determination of the molecular weight of an oil when dissolved in benzene is suggested as a method for standardising oils as regards their efficiency for absorbing vapours from gases. W. P. S.

Estimation of Alcohol in Spirituous Liquors. NAGENDRA CHANDRA NAG and PANNA LAL (*J. Soc. Chem. Ind.*, 1918, **37**, 290T).—A known weight of the alcoholic liquid is treated in a graduated cylinder with an excess of anhydrous potassium carbonate, 5 to 10% of water being added if the alcohol content is more than 90%; the mixture is then shaken and allowed to remain, or it may be subjected to centrifugal action. It separates into three layers: a lower layer of solid potassium carbonate, a middle layer of saturated potassium carbonate solution, and an upper layer of alcohol hydrate, $4C_2H_5 \cdot OH, H_2O$, which contains 94·061% of alcohol by volume or 91·089% by weight. The percentage quantity of alcohol in the sample is

$$(V + v \times 0·00275)[1 - 0·001068(t - 15·6)] \times 0·7936 \times 94·06 / W.$$

V is the volume, in c.c., of the alcohol hydrate observed, v the volume of the saturated potassium carbonate solution, t the temperature, W the weight in grams of the sample taken, 0·00275 is the solubility (in c.c.) of the alcohol hydrate per c.c. of the saturated potassium carbonate solution, 0·001068 the apparent coefficient of expansion of alcohol hydrate, and 0·7936 is the $D_{15·6}^{15·6}$ of absolute alcohol W. P. S.

A New Reaction for Acetylcarbinol. OSKAR BAUDISCH (*Biochem. Zeitsch.*, 1918, **89**, 279—280).—A dilute solution of acetylcarbinol in water containing sodium hydroxide is boiled for a few minutes with *o*-aminobenzaldehyde. The mixture is then cooled, acidified, and made alkaline again with sodium hydrogen carbonate. A fluorescent solution is obtained, from which 3-hydroxy-2-methylquinoline can be extracted by ether; on distilling off the ether, it is obtained as a white residue, which gives a deep red colour with ferric chloride in alcoholic solution. The alcoholic solution also gives a brilliant blue fluorescence on dilution with water. These two reactions are characteristic.

<div align="right">S. B. S.</div>

The Detection of Sucrose in Milk. G. D. ELSDON (*Analyst*, 1918, **43**, 292—293).—The most sensitive test for sucrose in milk is a modification of Gayaux's test, in which 15 c.c. of the milk are treated with 1 c.c. of $3N$-hydrochloric acid and 0·5 gram of resorcinol. On drying five drops of the resulting mixture on a white tile on the water-bath, a red coloration is obtained in the presence of as little as 0·02% of sucrose. <div align="right">C. A. M.</div>

Titration of Oxalic Acid by the Conductance Method. HERBERT S. HARNED and CLINTON N. LAIRD (*J. Amer. Chem. Soc.*, 1918, **40**, 1213—1218).—The electrical conductivity method affords a means of titrating a strong acid in presence of much weaker acids, and as a result of observations on the change of conductivity which occurs when a solution of oxalic acid is titrated with sodium hydroxide, it is found that the replacement of the first hydrogen atom by sodium is indicated very sharply by the conductivity. The influence of dilution on the sharpness of the change in the conductivity at the point at which the acid oxalate is formed has been examined, and it appears that the abruptness of the change increases with the dilution. The presence of carbonate in the hydroxide solution leads to high results when the conductance method is used in the estimation of oxalic acid. [See, further, *J. Soc. Chem. Ind.*, 653A.] <div align="right">H. M. D.</div>

Separation of Oxalic Acid from Tartaric Acid. ARMINIUS BAU (*Chem. Zeit.*, 1918, **42**, 425—426).—The solution, containing not more than 0·2% of oxalic acid, is treated with boric acid and one-fifth of its volume of calcium acetate solution, the mixture is kept in an ice-chest for forty-four hours, the precipitate of calcium oxalate then collected, washed, ignited, and the resulting calcium oxide titrated with $N/10$-hydrochloric acid. The volume of the filtrate and of the wash water must be noted; the solubility of calcium oxalate in the filtrate is equivalent to 3·42 mg. of oxalic acid per litre, whilst in the wash water it is equivalent to 4·64 mg. of oxalic acid per litre. The weight of oxalic acid found is corrected accordingly. The calcium acetate solution used is made by adding 500 c.c. of a solution of 330 grams of sodium acetate

in 300 c.c. of water to 25 grams of calcium chloride dissolved in 500 c.c. of 50% acetic acid; the mixture is kept at 7° for forty-eight hours, and then filtered. The amount of boric acid required to prevent the precipitation of calcium tartrate is at least 0·25 mol. of boric acid expressed in terms of tartaric acid, but a large excess of boric acid does not interfere. W. P. S.

Detection and Identification of Malonic Acid. BOUGAULT (*Ann. Chim. anal.*, 1918, **23**, 154—155).—Malonic acid condenses with cinnamaldehyde to form cinnamylidenemalonic acid, a yellow compound, m. p. 208°, practically insoluble in water (compare Rüber, A., 1904, i, 894). A mixture of 0·10 gram of malonic acid (or an equivalent quantity of its sodium or calcium salt), 15 drops of cinnamaldehyde, and 1 c.c. of acetic acid is heated at 100° in a sealed tube for ten hours. The mixture is then diluted with 15 c.c. of water, the solution saturated with sodium carbonate, filtered, and the filtrate acidified with hydrochloric acid; the yellow precipitate formed is collected, dried at 100°, and weighed. Each gram of malonic acid yields approximately 1·10 gram of cinnamylidenemalonic acid. Oxalic acid, succinic acid, citric acid, sodium chloride, or potassium sulphate do not interfere with the reaction. W. P. S.

Estimation of Indigotin. WILHELM HEINISCH (*Färber-Zeit.*, 1918, **29**, 183—184, 194—197).—The most suitable method for the estimation of indigotin in indigo is by titration with permanganate. Constant values for the oxygen consumed are only obtained by performing the titration in highly dilute solutions, from 1 part of indigotin in 20,000 of water, onwards. The constant value does not represent the oxidation of 1 molecule of indigotin by 2 atoms of oxygen with the formation of isatin, as was formerly supposed, but corresponds with the production of a complex oxidation product resulting from the action of 9 atoms of oxygen on 5 molecules of indigotin. Thus 262 parts of indigotin require 28·8 parts of oxygen, or, in other words, 1 mg. of potassium permanganate oxidises 2·3 mg. of indigotin. Using this ratio as the basis of the standard permanganate solution, it is possible to dispense with the usual practice of standardising the permanganate against a sample of indigotin of known purity; ferrous ammonium sulphate or an oxalate may be employed. The residual colour of the oxidised indigo solution ranges from yellow to reddish-brown, and the exact end-point cannot be established by ordinary direct titration. Accurate results may, however, be obtained by a process of colour matching. The titration is carried out simultaneously in duplicate nearly to the end-point, a faint green. Permanganate is then added alternately in small quantities to each of the solutions, which are compared against a white ground after each addition, until one sample shows no green tone and the other still retains a visible trace. [See, further, *J. Soc. Chem. Ind.*, 648A.] J. F. B.

Colour Reaction of Mercury Fulminate with Phenyl-hydrazine. A. LANGHANS (*Zeitsch. angew. Chem.*, 1918, **31,** i, 161—163).—On treating mercury fulminate with phenylhydr-azine, decomposition takes place, and on subsequently diluting the liquid with alcohol and adding a dilute acid, preferably sulphuric acid, a reddish-violet coloration is produced. This reaction may be used as a sensitive test for mercury fulminate. The dye can be extracted with chloroform, and its reactions indicate that it is pararosaniline. It is probable that the mercury plays a part in the reaction, since several mercury salts have been used in the preparation of rosaniline.

When phenylhydrazine is decomposed with chloride of lime, crystals of azobenzene and a yellowish-brown oil are produced. The oil consists of benzene, azobenzene, and aniline:

$$2NHPh \cdot NH_2 + 3O = 3H_2O + N_2 + NPh \colon NPh,$$
$$2NHPh \cdot NH_2 + 2O = 2H_2O + 2N_2 + 2C_6H_6.$$
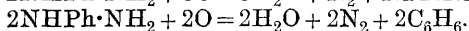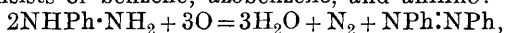
[See also *J. Soc. Chem. Ind.*, 1918, 637A.]   C. A. M.

Simple Apparatus for the Estimation of Urea in Blood. C. N. PELTRISOT (*J. Pharm. Chim.*, 1918, [vii], **18,** 73—80).—A small nitrometer is described for the estimation of nitrogen by the hypobromite method; it is constructed from a 30 c.c. glass bottle and a piece of graduated tubing, 8 cm. in length and 7 mm. in diameter.   W. P. S.

Estimation of Creatinine and Creatine in Blood. W. DENIS (*J. Biol. Chem.*, 1918, **35,** 513—516).—Accurate results for creatine and creatinine in the blood can be obtained by Folin's method (A., 1914, ii, 505) if the proteins are first precipitated by metaphosphoric acid.   H. W. B.

Detection of Ergotinine. LUDWIG WOLTER (*Chem. Zeit.*, 1918, **42,** 446).—An alcoholic solution of ergotinine containing 1 part in 1,240,000 gives a distinct reaction with the potassium mercuric iodide reagent for alkaloids. The yellowish-red zone, changing to violet and then to blue, given by a solution of ergotinine on the addition of sulphuric acid, is characteristic of this alkaloid (Tanret). In Rosenthaler's and in Keller's modifications of the test, a trace of ferric chloride is present. It is essential that all these tests, and especially that of Tanret, should be applied under definite conditions, and in particular that the solution of the alkaloid must not be too concentrated, or zones of other colours than blue will be obtained. The hypothesis that the coloration is due to oxidation was confirmed by the fact that a trace of hydrogen peroxide could replace ferric chloride in the test. With this modification, the reaction is rendered twice as sensitive as Tanret's original test. [See also *J. Soc. Chem. Ind.*, 1918, 671A.]

C. A. M.

The Value of Tanret's Reagent for the Detection of Quinine in Urine. G. PÉPIN (*Bull. Sci. Pharmacol.*, 1917, **24,** 337—338; from *Chem. Zentr.*, 1918, i, 955).—Tanret's reagent is

unsuitable for the detection of quinine in urine, since it yields precipitates which are soluble when warmed, even in the absence of proteins and alkaloids. H. W.

Isolation and Estimation of Small Quantities of Quinine in Urine. G. PÉPIN (*Bull. Sci. Pharmacol.*, 1918, **25**, 19—22; from *Chem. Zentr.*, 1918, i, 955).—The quinine is isolated by repeated extraction with small quantities of chloroform, purified, and dissolved in a few c.c. of water acidified with hydrochloric acid; the alkaloid is converted into a derivative which is soluble in water, and estimated by measuring the quantity of the solvent necessary for complete solution. The hydrate is suitable for amounts of 2—3 mg. and upwards, the picrate for quantities of less than 1 mg. Distinct fluorescence is observed with more than 1/20 mg. dissolved in water (2 c.c.). The presence of antipyrine and pyramidone alter the fluorescence and solubility of the picrate. H. W.

Estimation of Purine Bases in Food-stuffs. TH. VON FELLENBERG (*Biochem. Zeitsch.*, 1918, **88**, 323—336).—The author describes in detail the method employed, the bases being precipitated by copper sulphate and sodium hydrogen sulphite, and the nitrogen estimated in the precipitate. The purine content of a large number of foodstuffs is given. S. B. S.

Combined Estimation of Tyrosine and Uric Acid in the same Solution. E. HERZFELD and R. KLINGER (*Biochem. Zeitsch.*, 1918, **88**, 283—285).—Folin's phenol reagent is employed. It gives a colour twice as strong with tyrosine as with uric acid. The colour with the solution of the two substances is first estimated, then uric acid is destroyed by hydrogen peroxide and sodium hydroxide, then the phenol reagent is added again, under conditions specified, and the tyrosine alone is determined colorimetrically. S. B. S.

Detection of Bile Pigments in Serum. A. FOUCHET (*Compt. rend. soc. biol.*, 1917, **80**, 826—828; from *Physiol. Abstr.*, 1918, **3**, 246—247).—Proteins are precipitated by trichloroacetic acid, and the precipitate is yellow if bile pigments are present. On exposure to air, the precipitate becomes green, the oxidation to biliverdin being accelerated by the addition of ferric chloride. The method may be used colorimetrically. S. B. S.

Modification of Grimbert's Method for the Detection of Biliary Pigments in Urine. A. FOUCHET (*J. Pharm. Chim.*, 1918, [vii], **18**, 19—20).—Ten c.c. of the urine are treated with 3 c.c. of 10% barium chloride solution, the mixture submitted to centrifugal action, the sediment washed, and then mixed with 1 c.c. of a reagent consisting of trichloroacetic acid, 3 grams, ferric chloride solution, 2 c.c., and water, 20 c.c. A green coloration develops within a few minutes if biliary pigments are present. The sensitiveness of the test is about 1 in 50,000. W. P. S.

Detection of Methylene-blue in Urine. L. TRIBONDEAU (*Compt. rend. soc. biol.*, 1917, **80**, 882; from *Physiol. Abstr.*, 1918, **3**, 264).—Urine is acidified with acetic acid, fragments of thymol are added, and the mixture is boiled. Thymol collects on the surface, carrying with it the pigment.   S. B. S.

Approximate Estimation of Proteins in Physiological Fluids. ROKURO NAKASEKO (*Mem. Coll. Sci. Kyoto.* 1918, **3**, 93—112).—A preliminary account is given of an acidimetric method for estimating proteins by precipitating with picric acid in the presence of hydrochloric acid, a given diminution of acidity after precipitation corresponding with a given amount of protein. A modification of Esbach's method is also described in which the precipitation by picric acid is carried out in the presence of $N/20$-hydrochloric acid instead of citric acid. A modification of Roberts and Stolnikov's application of the Heller test is also described.   S. B. S.

Hydrolysis of Proteins in the Presence of Extraneous Materials and the Origin and Nature of the " Humin " of a Protein Hydrolysate. ROSS AIKEN GORTNER (*Science*, 1918, (N.S.), **48**, 122—124. Compare A., 1916, i, 681; Hart and Sure, A., 1917, ii, 111).—The author points out that the results obtained by McHargue (this vol., ii, 280) are incorrect, because he has failed to recognise that the insoluble residue obtained on digestion of caseinogen is humin, and consequently he has omitted to take into account the nitrogen in this fraction when calculating the distribution of nitrogen in the protein. Hence the general conclusion is that an accurate estimate of the distribution of nitrogen in a feeding stuff cannot be obtained by a direct application of the Van Slyke method of analysis, even when the duration of the hydrolysis is limited to twelve to fifteen hours.   H. W. B.

Acetic–Sulphuric Acid Test for Albumin. R. LEONE (*Policlinico*, 1918, **25**, 224; from *Physiol. Abstr.*, 1918, **3**, 223).— The test depends on the precipitation of protein by a reagent prepared by adding 100 drops of glacial acetic acid and 100 drops of a 25% solution of sulphuric acid to 100 c.c. of a 10% solution of potassium dichromate.   S. B. S.

Protein–Sugar, its Estimation. H. BIERRY and (MME.) L. RANDOIN-VANARD (*Soc. Biol.*, May, 1918; from *J. Pharm. Chim.*, 1918, [vii], **18**, 54).—The following method is suggested for the hydrolysis of the protein–sugar compound found in blood. Fifty c.c. of the blood are mixed with 50 c.c. of 0·2% sodium chloride solution, diluted with 90 c.c. of water, and 4 c.c. of sulphuric acid mixed previously with 10 c.c. of water are added; the mixture is then heated in an autoclave at 120° for forty minutes.   W. P. S.

General and Physical Chemistry.

Spark and Arc Spectra of Gallium, Indium, and Zinc. L. M. Dennis and J. Allington Bridgman (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—See this vol., ii, 456.

Absorption Spectra of the Blue Solutions of certain Alkali and Alkaline Earth Metals in Liquid Ammonia and in Methylamine. G. E. Gibson and W. L. Argo (*J. Amer. Chem. Soc.*, 1918, **40**, 1327—1361. Compare *Physical Rev.*, [N.S.], 1916, **7**, 33).—In a previous paper (*loc. cit.*), it was shown that dilute solutions of sodium and magnesium in liquid ammonia had identical absorption spectra. The similarity was explained as due to the dissociation of the metal atoms into electrons partly combined with the solvent, and into cations which are also present in liquid ammonia solutions of salts of the metal. The present paper contains an account of further work on the same subject. The absorption spectra of solutions of lithium, potassium, and calcium in liquid ammonia, and of lithium, sodium, potassium, cæsium, and calcium in methylamine, have been measured. With the possible exception of calcium, the solutions in liquid ammonia have the same absorption spectra as those previously measured. In methylamine, the absorption spectra are entirely different from those in liquid ammonia, a marked absorption maximum appearing which is absent in liquid ammonia solutions. The maximum lies at $650\,\mu\mu$, and is independent of the nature of the metal. In liquid ammonia, the absorption index is independent of temperature, but in methylamine a marked negative temperature coefficient is observed in every case examined, the absorption index diminishing approximately 1% for a rise of 1°. In liquid ammonia, the absorption index is proportional to the total concentration of the metal. In methylamine, the same is true at the position of the band maximum, but at shorter wave-lengths deviations are observed, the absorption increasing more rapidly than Beer's law demands with increase in the concentration. The ratio of the absorption index at $650\,\mu\mu$ to that at $530\,\mu\mu$ increases not only with increasing concentration of the metal, but also with increasing concentration of the reaction product of the metal with methylamine, and probably also with increasing temperature. The experimental results are explained by the following hypothesis. The colour in all cases is due to electrons combined with the solvent. In ammonia, the dissociation of the metal into electrons is nearly complete, and the concentration of electrons uncombined with solvent is negligible compared with that of the solvate electrons. In methylamine, the concentration of un-ionised metal is no longer negligible, and is responsible for the increased absorption at the shorter wave-lengths; further, the solvation of the electrons in methylamine is incomplete and diminishes as the temperature is increased. J. F. S.

Determination of the Constitution of Coloured Substances from their Absorption Spectra. F. KEHRMANN and MAURICE SANDOZ (*Helv. Chim. Acta*, 1918, **1**, 270—277).—A résumé of work previously published on the relationships between colour and constitution.   J. F. S.

Absorption of Light and Size of Particles in Disperse Systems. NILS. E. PIHLBLAD (*Inaug. Diss.*, Upsala, 1918, pp. 85; from *Chem. Zentr.*, 1918, ii, 92—93).—Mainly an account of work which has been published previously (A., 1909, ii, 277, 561, 723; 1910, ii, 946; 1913, ii, 2; 1917, ii, 557). Spectrophotometric observations of a silver hydrosol with very small particles show that the absorption increases towards the region of shorter wavelength, and that the maximum is not attained at $\lambda = 400 \mu\mu$; with larger particles, the maximum lies in the blue-green and passes finally into the yellow region. All the silver hydrosols investigated have a second, better marked maximum in the ultraviolet.

A colloidal solution of Butter-yellow O was obtained by adding water to an alcoholic solution of the dye, the size of the particles being controlled by varying the concentration of the alcoholic solution. As the size of the particles decreases, the absorption approximates to that of a molecular solution.   H. W.

The Stratification of Liquid Layers. JEAN PERRIN (*Ann. Physique*, 1918, [ix], **10**, 160—184).—A repetition and extension of Johonnott's work (compare *Phil. Mag.*, 1906, 751) on the "black spots" in the films of soap bubbles. The author shows that the number of these coloured regions of uniform thickness may become very great after the addition of colouring matters, such as uranin or æsculin, the soap films assuming a stratified structure. Light favours the evolution of the film, the particular portion of the spectrum which is most active being that which is absorbed by the colouring material in the film. Similarly, rise in temperature favours the stratification. Stratification can also be observed in the films from "soapy" water obtained with rosin. The author suggests a method for enumerating these coloured areas, and shows that their number is independent of the substances added to the water (soap or rosin). In a stratified liquid film, the thickness of each area is a whole multiple of an elementary thickness of about 5 millimicrons.   W. G.

Fluorescence. JEAN PERRIN (*Ann. Physique*, 1918, [ix], **10**, 133—159).—A theoretical discussion of the subject. The emission of fluorescence implies the destruction of the fluorescent substance, and it is probably only at this moment of destruction that the molecules are fluorescent. Variations of temperature and viscosity do not exert any marked influence on the fluorescence of organic substances. This molecular fluorescence resembles in character the atomic fluorescence or phosphorescence excited by the cathode rays,

X-rays, or α-, β-, and γ-rays in inorganic substances. The optimum concentration giving the maximum fluorescence depends on the thickness of the liquid layer studied, but is in all cases less than 20%. Beyond a certain dilution, the fluorescence of a given mass remains constant, the fluorescent power thus having a well-defined limiting value. Each transformation of a fluorogen molecule causes the emission of a quantity of light independent of the exciting illumination and of the concentration, and a formula is given for the calculation of the energy radiated by fluorescence.   W. G.

Crystalloluminescence.   HARRY B. WEISER (*J. Physical Chem.*, 1918, **22**, 480—509).—After an historical survey of the work done on this subject, the author describes a series of experiments on sodium chloride, potassium chloride, potassium bromide, potassium iodide, sodium bromide, and sodium iodide.   The effects are produced by precipitating the salts in question by means of alcohol, and in the case of all but sodium iodide with the corresponding halogen acid of various concentrations.   The effect of modifying the conditions, by stirring during precipitation, varying the temperature, and increasing the viscosity of the solution by the addition of a colloid (gelatin) and by the addition of a non-electrolyte (sucrose), is also studied.   It is shown that crystalloluminescence is caused by chemical action.   It is also probable that all cases of triboluminescence are due to chemical action.   The luminescent reaction is probably identically the same in the case of substances that show both crystalloluminescence and triboluminescence; the only difference is in the actual way in which the reaction is brought about.   The specific reaction which produces crystalloluminescence of the alkali haloids is the recombination of the ions with the formation of non-dissociated salt.   In the salts mentioned above, crystalloluminescence was observed in every case save those of sodium bromide and iodide, and in every case the conditions were determined for obtaining the maximum effect. The maximum intensity of the crystalloluminescence results under conditions which favour the accumulation throughout the solution of the largest possible concentration of ions in excess of the equilibrium concentration of ions and allow the luminescent reaction, once started, to go rapidly to completion.   The actual conditions differ with different salts.   The crystalloluminescence of sodium chloride is bluish-white in colour, and not white as stated by Bandrowski (A., 1895, ii, 66).   The colour of the luminescence produced when sodium is burned slowly in air is similar to, but slightly bluer than, the crystalloluminescence of sodium chloride. The difference is due to the specific effect of the anion.   J. F. S.

Some Properties of the Active Deposit of Radium.   S. RATNER (*Phil. Mag.*, 1918, [vi], **36**, 397—405).—The phenomenon of the spreading of the active deposit of radium after deposition on a disk, as though the deposit was slightly volatile, has been investigated, and some remarkable results have been obtained, without

disclosing the nature of the phenomenon, but revealing a grave source of error in certain investigations. A disk was mounted in air opposite the plate coated with the active deposit and charged to a high potential, positively to the plate, to prevent recoil phenomena when radium-A was present. It always acquired some of the same active deposit as that on the plate. Washing or slightly heating the plate reduces the loss of active deposit from it enormously. When the plate is only exposed to the emanation for a short time, in order to coat it with the active deposit, the proportion of active deposit it loses is much increased. A plate exposed to the emanation for a fraction of a second loses as much radium-A as if exposed for several minutes, and for these very short exposures, the amount of radium-A lost is comparable with the amount of radium-B lost by recoil. For radium-$B + -C$, from 0·1 to 0·04% is given up, sufficient except in special circumstances to mask the recoil of radium-C_2.

In certain cases, the time in which the quantity of active matter reaching the disk per unit of time falls to half-value was found. For radium-A the results were most regular, the time always being 1·4 minutes. If the quantity lost were proportional to the quantity of active matter present on the disk, this time should, of course, have been three minutes. Exposing the active deposit to a violent stream of gas from a cylinder at 80 atmospheres did not reduce appreciably the subsequent loss of active matter, and the physical and chemical conditions of the surface on which the active deposit had been formed had no influence. F. S.

The Measurement of the Radium Emanation in the Atmosphere. Josef Olujić (*Jahrb. Radioaktiv. Elektronik.*, 1918, **15**, 158—193).—A simplified method of determining the amount of radium emanation in the atmosphere by condensation with liquid air is described, and the results of measurements extending over several years, both by absorption and condensation methods, given. A connexion has been traced in Freiburg (Switzerland) between the amount of the radium emanation in the atmosphere and the meteorological conditions. The mean emanation content was found to be 131×10^{-18} curie per c.c. With a maximum of 305 and minimum of 54, results somewhat higher than these have been found by numerous other investigators in various localities. F. S.

The Radium Content of Water from the China Sea. J. R. Wright and G. W. Heise (*Philippine J. Sci.*, 1918, **13**, [A], 49—56).—Tests on a single large sample of sea-water, collected from a depth of 2 metres in the open sea, 8 kilometres from the entrance to Manila Bay, were made by the Chauval absorption method comparatively against a standard radium solution. The mean of these determinations gave the value as only $0·2 \times 10^{-12}$ gram of radium per litre, whereas a test by Joly's direct method gave a value only one-half of this. These values are much lower

than those found by other investigators for sea-water from other localities. **F. S.**

Radioactivity of Italian Minerals. L. FRANCESCONI, N. GRANATA, A. NIEDDU, and G. ANGELINO (*Gazzetta*, 1918, **48**, i, 112—113).—Of a number of Italian minerals from different localities, the following are found to be radioactive: pyromorphite, the radioactivity of which varies with the physical characters, especially with the colour; wulfenite and chrysocolla. Certain minerals of lead are found to retard the discharge of the electroscope. Radioactivity has also been observed with malachite from Carrisal (Chile) and with galena (with litharge) from Biokaha (Argentine).

T. H. P.

Knowledge and Interpretation of Isotopic Varieties of Lead. K. FAJANS (*Zeitsch. Elektrochem.*, 1918, **24**, 163—169).— In conjunction with A. Nadai and F. Richter, lead was separated from a Norwegian thorite from Langesundfiord, analysing 30·1% thorium, 0·45% uranium, and 0·35% lead, in which the thorium to uranium ratio is 75, and for which the atomic weight of lead, if derived wholly from the uranium and thorium, should be between 207·97 and 208·00. The atomic weight of this lead was found by O. Hönigschmid to be 207·90±0·013, which is the highest value yet experimentally found, that prepared from Ceylon thorite, with the thorium to uranium ratio 55, by Soddy, having the atomic weight 207·77. The small difference between the experimental and calculated values, if significant and due to the thorium lead not being completely stable, shows that the half-period of the thorium lead must be at least $1·7 \times 10^8$ years.

The question is discussed whether, in the various kinds of lead having atomic weights between 206 and 208, there are other isotopes than those derived from uranium and thorium, and especially whether common lead, with atomic weight 207·2, is a mixture of these isotopes or a third distinct isotope. If uranium minerals of the same geological age are compared, the ratio $\dfrac{206·0}{\text{Pb}}\Big/\text{U}$ should be constant, and if the variation of the atomic weight of the lead above the value 206·0 is due to the admixture of common lead $\left(\dfrac{207·2}{\text{Pb}}\right)$, the β-activity of the lead, which is due to Ra-*D* + -*E*, and which is a measure of the $\dfrac{206·0}{\text{Pb}}\Big/\text{U}$ ratio, should decrease as the atomic weight of the lead increases. Three specimens of lead from Joachimsthal pitchblende, the atomic weights of which were I 206·405, II 206·61, III 206·73, were found to possess β-activity, calculated back to the time of the separation of the lead from the mineral, in the ratio 1 : 0·639 : 0·55. It is shown that these figures are in fair agreement with the view that the lead is a mixture of the uranium isotope with common lead, and there are no grounds for assuming the existence of more than three isotopes, uranium lead 206·0, thorium lead 208·0, and common lead 207·2. **F. S.**

The Refractive Index and Solubilities of the Nitrates of Lead Isotopes. THEODORE W. RICHARDS and WALTER C. SCHUMB (*J. Amer. Chem. Soc.*, 1918, **40**, 1403—1409).—The nitrates of lead chosen were (1) from "test-lead" free from silver and tin, and (2) from pure Australian uranio-lead nitrate (compare Richards and Hall, A., 1917, ii, 230) containing lead of atomic weight 206·42. The refractive indices, determined by means of the Abbe crystal refractometer, using a solution of sulphur in methylene iodide of refractive index 1·79 as the medium between the face of the crystal and that of the glass prism of the refractometer, proved to be $n_D = 1·7814$ for each at about 20°, no systematic difference between the individual measurements being detected. The solubilities were determined at 25·02°, after twenty-four hours' shaking in the thermostat, by weighing the filtered solution, then evaporating with sulphuric acid, and heating the lead sulphate to constant weight at 350°. The following table gives the results:

	Common lead.	Uranio-lead.	Difference. per cent.
Grams $Pb(NO_4)_2$ per 100 grams solution	37·342	37·280	—
Grams $Pb(NO_4)_2$ per 100 grams water	59·597	59·439	0·26
Grams Pb per 100 grams water	37·281	37·130	0·41
Molal solubility per 1000 grams water	1·7993	1·7991	—

Thus no difference has been found in the refractive indices and molal solubilities, showing that, as in other cases, the weight or mass of the two kinds of lead studied is their prime distinguishing feature.   F. S.

The Ratio of Mesothorium to Thorium. HERBERT N. McCOY and LAWRENCE M. HENDERSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1316—1326).—The convention applies throughout that "1 mg. of mesothorium" is the quantity of mesothorium-1 + -2 in equilibrium which has a γ-ray activity equal to that of 1 mg. of radium in equilibrium with its first four products. It further appears that the γ-activity was measured through 2·03 mm. of lead + 1·32 mm. of brass. The result of the research was that "1 mg. of mesothorium" is in equilibrium with 19 kilograms of thorium in minerals, or 1 gram of thorium is in equilibrium with $0·524 \times 10^{-4}$ "mg. of mesothorium." It is important to note that the last ratio is only one-sixth as great as the ratio of radium to uranium, namely, $3·23 \times 10^{-4}$ mg. of radium for 1 gram of uranium.

The total γ-activity of thorianite due to thorium, correcting for the absorption of the rays in the mineral and deducting that due to the contained radium, was found to be equal to that of 1 mg. of radium for 6·85 kilograms of thorium, in agreement with a former result by Eve, which indicates that 36·3% of the total γ-activity of thorium is due to mesothorium and the remaining 63·7% to thorium-D.

The method followed, since it was not possible to separate sufficient of the minerals to determine the γ-rays of mesothorium

directly, was to determine the β-activity of the mesothorium in arbitrary units, and then the ratio of the β-activity in these units to the γ-activity in terms of that of a standard radium preparation, for a specimen of pure mesothorium.

The results for various minerals and various methods of separating the mesothorium varied between 0.484 and 0.559×10^{-4} for the ratio in question, the mean value 0.524×10^{-4} being taken, as already given.   F. S.

The Electrical Conductivity of Acids and Bases in Aqueous Solutions. Jnanendra Chandra Ghosh (T., 1918, **113,** 790—799).—The equation which the author has previously developed (compare this vol., ii, 215, 348), showing the relation between equivalent conductivity and dilution, does not hold in the case of aqueous solutions of strong acids and strong bases, whereas it is found to be valid, for strong acids, in alcoholic solutions. It is well known that in aqueous solution the hydrogen and hydroxyl ions possess abnormally large mobilities, and in explanation of this the author assumes that the electricity is partly carried by the ordinary process of convection and partly propagated through water molecules undergoing alternate dissociation and recombination. On this assumption, it would follow that the real ionic mobilities of hydrogen and hydroxyl ions are less than those usually calculated from experimental data. Assuming that in the case of an aqueous solution of hydrochloric acid, for example, the observed ratio of μ_v/μ_∞ is not a real expression for the activity coefficient, it is deduced that the real mobility of the hydrogen ion, $U_{H^\cdot}$, is given by the equation $U_{H^\cdot} = \{\mu_\infty - \mu_v - (1 - \alpha)U_{Cl'}\}/(1 - \alpha)$, where α is the activity coefficient and μ_∞ is given by the expression $\mu_\infty = U_{H^\cdot} + U_{Cl} + C_1$, C_1 being a constant independent of the dilution and expressing the conductivity due to the alternating dissociation and recombination of the water molecules and constituent ions. The experimental data on the conductivity of acids must always yield the same values of C_1 and $U_{H^\cdot}$, as calculated from the above equations, and this is shown to be the case for aqueous solutions of hydrochloric and nitric acids, the values being respectively 197.8 and 152.4 for the former acid and 198.8 and 151.3 for the latter. In a similar manner, the value for U_{OH} is found to be 109 in the case of potassium hydroxide, C_1 being 66. Using these values, μ_v can be calculated for any dilution, and it is shown that the agreement between calculated and observed values is very close for aqueous solutions of hydrochloric, nitric, naphthalene-β-sulphonic and toluene-p-sulphonic acids, and for potassium hydroxide.

Based on the consideration that only free ions, that is, ions which by virtue of their kinetic energy can overcome the force of electrostatic attraction, have the capacity of regenerating undissociated molecules, a modified Ostwald equation, $(\alpha x)^2/(1 - x)V = K$, is developed for weaker electrolytes where the degree of dissociation

is less than one; x is the fraction of a gram-molecule of acid which has undergone dissociation into ions, and a is the activity co-efficient at the ionic concentration x/V. This equation becomes identical with Ostwald's dilution law for very weak electrolytes, where a is always very nearly equal to one, and it is shown that it gives very concordant values for the equilibrium constant in the case of "transition" electrolytes, such as cyanoacetic, o-nitrobenzoic, dichloroacetic, and trichlorobutyric acids, where Ostwald's equation is not applicable. T. S. P.

Planck's Formula for the Potential Difference between Solutions and the Values of certain Important Cells.

H. A. FALES and W. C. VOSBURGH (*J. Amer. Chem. Soc.*, 1918, **40**, 1291—1316).—The Planck formula by which contact potentials may be calculated has been examined and tested against the measured contact potentials obtained by the authors according to a new plan, which is based on the absence of a contact potential between solutions of potassium chloride. It is shown that this formula does not represent fact for the liquid junctions xMKCl—$1\cdot0M$HCl and xMKCl—$0\cdot1M$HCl, where x ranges from $0\cdot1$—$4\cdot1$. It is further shown that at $25°$ no contact potential exists between a saturated solution of potassium chloride ($4\cdot1M$) and hydrochloric acid solutions ranging in concentration from $0\cdot1M$—$1\cdot0M$. In an *E.M.F.* combination having a contact potential as one of its component *E.M.F.*'s, the diffusion across the liquid junction of the one liquid into the other brings about a decrease in the magnitude of the contact potential, and this decrease may amount to as much as one-tenth of the initial magnitude of the contact potential. For this reason, combinations having only very small or zero contact potentials should be used for precise measurements. As the result of the measurement of some thirty combinations at $25°$, the following values are given for the important half-elements, and an accuracy of $\pm0\cdot0002$ volt is claimed: Hg|HgCl|$1\cdot0M$KCl||$0\cdot5648$ volt, Hg|HgCl|$1\cdot0M$HCl||$0\cdot5567$ volt, Pt|H$_2$(1 atm.)|$1\cdot0M$HCl|| $0\cdot2777$ volt, Hg|HgCl|$0\cdot1M$KCl||$0\cdot6168$ volt, Hg|HgCl|$0\cdot1M$HCl|| $0\cdot6168$ volt, and Pt|H$_2$(1 atm.)|$0\cdot1M$HCl||$0\cdot2179$ volt. A new form of vessel in which to make calomel electrodes is described. This has the advantage that the liquid may be drawn off and re-placed without disturbing either the mercury or the electrode. J. F. S.

Occlusion of Hydrogen and Oxygen by Metal Electrodes.

EARLE A. HARDING and DONALD P. SMITH (*J. Amer. Chem. Soc.*, 1918, **40**, 1508—1531).—A continuation of work previously pub-lished (Smith and Martin, A., 1917, ii, 64) on the change of resist-ance of platinum wires brought about by the occlusion of hydrogen. In the present paper, the effects on resistance by the occlusion of oxygen and hydrogen in platinum, palladium, iron, and tantalum wires have been studied, together with dimensional changes of the wires. The results confirm the conclusions put forward in the

earlier paper. This conception is that hydrogen, when evolved electrolytically, enters the metal of the electrode in a transitional form in the cases in which the gas is largely occluded, and then passes gradually into another form which has the opposite effect on the resistance. Indications have been obtained that the behaviour of oxygen is similar to that of hydrogen. The quantity of the transitional form present when continued electrolysis has led to a steady state of resistance is dependent on the current density. In the case of hydrogen, it may reach very high values, and the consequent diminution of electrical resistance is also large in the case of hydrogen, but much smaller in that of oxygen when the current densities are the same. The transitional form of hydrogen appears to be responsible for the major part of the change of dimensions produced in palladium by electrolytic occlusion. In the more persistent, or "alloy form," the hydrogen is firmly held by palladium up to a critical temperature, which has not been determined, but which probably lies not far from 300°. At this temperature, hydrogen begins to be evolved freely.

J. F. S.

The Replacement of Platinum in Apparatus for Electrolysis. PAUL NICOLARDOT and JEAN BOUDET (*Bull. Soc. chim.*, 1918, [iv], **23**, 387—391).—Alloys of gold and platinum containing from 12·5—25% of platinum were examined as to their suitability for use as electrodes under varying conditions, but it was found that they varied too much in weight during electrolysis in alkaline solution or in the presence of sulphides and sodium cyanide. The authors recommend the use of an alloy of gold, silver, and copper in the proportions 920:50:30, and coating the electrodes with a thin layer of platinum (0·005 gram per cm.²).   W. G.

Electrolytic Potential of Alloys. Antimony-Bismuth, Lead-Thallium, Thallium-Antimony. E. BEKIER (*Chemik Polski*, 1917, **15**, 119—131; from *Chem. Zentr.*, 1918, i, 1000—1001).—The measurement of the electrode potential was effected according to Poggendorf's compensation method. The cells used were of the H-form; in one limb was placed the electrode under investigation, in the other an electrode of the less noble metal. Solutions of salts of the less noble metal were employed as electrolytes.

System Bismuth–Antimony.—The electrolyte consisted of a saturated solution of potassium antimonyl tartrate. The results show the existence of a continuous series of mixed crystals.

System Thallium–Lead.—Electrolyte, thallous chloride solution. Mixed crystals are shown to be present. The region is, however, greater than that indicated by thermal analysis, and extends from 100 to 12% of lead; between 0 and 12% of lead, mixed crystals do not exist.

System Thallium–Antimony.—Electrolyte, thallous chloride.

20*

Equilibrium between electrode and electrolyte is rapidly attained except in the case of electrodes with high antimony content. Alloys containing 0—16·4% of antimony show the potential of thallium, and therefore contain the free element; alloys corresponding with the formulæ $SbTl_4$ and $SbTl_3$ also contain free thallium. Alloys containing between 16·49 and 90% of antimony show a constant potential, and thus contain a compound of the two elements. Alloys containing 90% or more of antimony show a rapid decline in potential, which points to the existence of mixed crystals of the compound and antimony.   H. W.

Measurement of the Velocity of Electro-osmosis. S. GLIXELLI (*Chemik Polski*, 1917, **15**, 111—118; from *Chem. Zentr.*, 1918, i, 1107—1108.   Compare Perrin, A., 1904, ii, 8).—The apparatus (see Fig.) consists of two parts connected by a ground joint, S.   The diaphragm, which can be gelatinous or pulverulent, is placed in the tube between A and B.   Experiments have shown that a diaphragm of moderately dilute silica gel can withstand slight hydrostatic pressure, so that a cotton-wool support is un-

necessary.   A large number of substances may be used as diaphragm with the exception of certain sensitive gels, and of such as are in a condition of peptisation.   The portions of the apparatus between A and D and B and E, which connect the diaphragm with the electrodes, the open tube O, and the capillary tube with stopcock C, are filled with the substance under investigation. The electrode vessels, DJ and EK, are completely filled with copper sulphate solution, into which the copper electrodes M and N dip. The current is sent through the non-polarisable electrode.   The tube is filled through F.   When the electrode vessels have been filled, the diaphragm, which has been repeatedly washed with the electrolyte under investigation, is introduced into AB.   The solution under investigation is added through O and C.   A capillary tube, P, serves to measure the volume of the liquid carried forward by the current.   As soon as the liquid has attained equilibrium in O and in the measuring tube, C is closed and A, B, D, and E are opened; the apparatus is then ready for use.   Electro-osmosis also occurs through the closed cock C, but to an extent which may be neglected.   H. W.
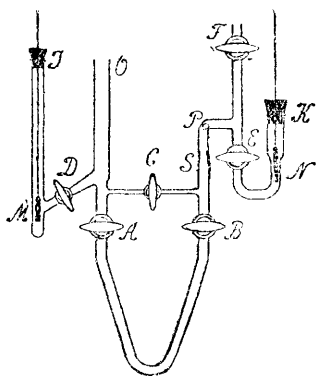
Significance of the Magnetic Susceptibility of Solutions. Nuclear State of Solutions. I.   A. QUARTAROLI (*Gazzetta*, 1918, **48**, i, 79—101).—Further evidence is advanced (compare A., 1916, ii, 413) confirmatory of the view that support for Weiss's

magneton theory cannot be obtained from data regarding dissolved salts. By means of the differential method devised for the estimation of magnetic salts in solution (this vol., ii, 458), and making use of a solution of nickel chloride, carefully freed from cobalt, as standard solution, the author has measured the magnetic susceptibilities of various ferric, ferrous, manganese, cobalt, chromium, and copper salts at different dilutions. The results show that, on the assumption that that of nickel chloride remains constant, in general the molecular susceptibility decreases slowly with increase of the dilution; it is, however, impossible by extrapolation to calculate a limit, since the diminution appears to become rather more rapid as dilution progresses. This holds true even, as is probably the case, if the molecular susceptibility of nickel chloride itself undergoes some diminution on dilution.

The differential method referred to also allows of the alteration of the susceptibility by centrifugation being detected in solutions containing 1 part of ferric or manganese chloride or sulphate in 5000 parts of water, or 1 part of nickel chloride or sulphate per 1000 parts of water.

From the results obtained, the conclusion is drawn that there exists a discontinuity in the relation connecting the variation in concentration with the force tending to oppose such variation, an almost infinitesimal change of concentration counterbalancing appreciable definite forces acting to increase the change. It is suggested that the state of solution represents a special "nuclear" condition, in which, although the characteristic external attributes of liquids are not lost, attractions emanating from the centre of the nuclei (molecules of solute) determine regions of greater rigidity.

The explanation of various phenomena by means of this hypothesis is discussed.   T. H. P.

Atomic Heat, Volume Elasticity, and Characteristic Frequency of Monatomic Metals. A. L. BERNOULLI (*Helv. Chim. Acta*, 1918, **1**, 278—288).—A theoretical paper in which it is shown that, on the assumption that the atoms or molecules are solid bodies which under the action of distant repulsive forces set up characteristic vibrations, Magdeburg and others were able to evolve a quantitative relationship between the vibration number and the elastic cubic compressibility, whilst, in opposition to this, the Einstein equation shows that the work of compression only increases the kinetic energy of rotation of the molecule, that is, it does not work against the repulsive molecular distant action. Without any further assumption, this leads to a new proportionality factor from this equation which gives a much better agreement between the value of the ultra-red characteristic vibration obtained from the compressibility and that obtained from the specific heat, always assuming that the material is perfectly elastic. It is also shown that the compressibility may be calculated from the values of the vibration numbers, and that for the metals

20*—2

copper, aluminium, and lead the divergence from Dulong and Petit's law may be calculated from compressibility measurements at stated temperatures.   J. F. S.

The Solid State. UGO PRATOLONGO (*Gazzetta*, 1918, **48**, i, 193—237).—If a solid is regarded as a congeries of atomic systems which are in static equilibrium and in which the distribution of energy follows the laws defined by the doctrine of Gibbs, the author shows that it is possible to give a satisfactory representation of the solid and of its characteristic properties. The latter are divided into two groups: (1) Those which vary as a function of the modulus of energetic distribution θ in accordance with the relation $\omega = c^{(\psi - \epsilon)/\theta + \text{const.}}$ where ω indicates one of the properties of the group and ψ is the mean energy of the systems constituting the whole; this group comprises the specific heat, thermal conductivity, expansibility, and magnetic susceptibility. (2) The thermal radiation, electrical conductivity, and magnetic induction, which are connected with variations of θ by a relation expressed rigorously by Planck's formula, $\tau = (e^{(\psi - \epsilon)/\theta} - 1)^{-1}$, or approximately by Rayleigh's formula, $\tau = \theta e^{(\psi - \epsilon)/\theta} + \text{const.}$, where τ represents one of the properties of the group.

The relation between the modulus of distribution θ and the temperature T or the magnetic field H is, for each of the properties considered, one of simple equality. In the phenomena of thermal radiation, electrical and thermal conductivity, and magnetic susceptibility, the relation $\theta = T$ is found. In the case of specific heats, the relation has the form $\theta = T\gamma$, whilst with magnetic induction it is expressed by $\theta = H$ or $\theta = H^2$, according as the induction is due to fields of high or low intensity. The reasons of such multiplicity of relations lies evidently in the intimate mechanism of the energy exchanges between the atomic systems, but are as yet unknown.

In each of the phenomena of the first group, considered separately, there participate only those atomic systems the energy of which has reached a critical value ϵ; the latter is different for the different physical phenomena and characteristic for every atomic or molecular species, being connected with the atomic frequency according to a general relation. Between the limits of approximation of the methods of investigation, the difference between the mean atomic energy and the critical energy, $(\psi - \epsilon)$, which may be termed the relative critical energy, appears to be proportional to the atomic frequency.

As far as the available experimental data go, the curves representing the specific heats as a function of the temperature seem to be grouped in two distinct types; the fundamental difference thus indicated is apparently related to the crystalline form.

The phenomena of the second group are functions of the energy content of the whole system considered.   T. H. P.

Still for the Continuous Preparation in Quantity of Water of High Purity. HAL W. MOSELEY and ROLLIN G. MYERS (*J. Amer. Chem. Soc.*, 1918, **40**, 1409—1411).—The apparatus

consists of two 5-litre, round-bottomed Pyrex glass flasks which are set at an angle of 60°. The first flask is fitted with a pressure tube, a supply tube, by means of which ordinary distilled water is admitted, and an exit tube which leads to the bottom of the second flask. The second flask is fitted with a steam delivery tube and an exit tube which carries a trap. The exit tube of the second flask is connected to a Findlay adapter, which in its turn is attached to a tin condenser. The water in the first flask contains 10% of potassium dichromate and 5% of sulphuric acid, whilst that in the second flask contains barium hydroxide. Both flasks are heated, and the apparatus is capable of furnishing continuously about a litre of very pure water in an hour. The stoppers used in the flasks are made of Portland cement, whereby the use of rubber and cork is rendered unnecessary. J. F. S.

The System : Acetone–Ethyl Ether. JITSUSABURO SAMESHIMA. (*J. Amer. Chem. Soc.*, 1918, **40**, 1482—1503).—The author has determined the vapour density of ethyl ether and acetone by a slightly modified form of Menzies' method at 25°, and finds that at this temperature both vapours are non-associated. The densities of mixtures of acetone and ethyl ether have been determined over the whole range of composition 0—1 molecular fractions at 25·04°. Series of vapour pressure determinations of binary mixtures of the same substances and of the simple substances have been determined at 20° and 30°. It is shown that in liquid acetone the reaction $3C_3H_6O \rightleftharpoons (C_3H_6O)_3$ takes place. The vapour pressure of the acetone–ethyl ether system, the heat of vaporisation of acetone, the heat of mixing acetone and ethyl ether, and the volume contraction on mixing were calculated from the experimental data, and the values compared with directly observed results. The agreement is fairly good and affords confirmation of Ikeda's conclusions in connexion with quasi-ideal solutions (A., 1908, ii, 932). J. F. S.

The System : Benzene–Carbon Disulphide. JITSUSABURO SAMESHIMA (*J. Amer. Chem. Soc.*, 1918, **40**, 1503—1508).—A series of vapour pressure determinations of mixtures of benzene and carbon disulphide has been carried out at 20°, 25°, and 30°, and the results plotted. From the results, the heat change on mixing and the change of free energy have been calculated for various mixtures at 25°. J. F. S.

Fractional Distillation Tube. W. G. FRIEDEMANN (*J. Amer. Chem. Soc.*, 1918, **40**, 1411).—A fractional distillation column can be made by connecting together Kjeldahl trap bulbs by means of rubber tubing. J. F. S.

Critical Temperature of Mercury. (MISS) JULIE BENDER (*Physikal. Zeitsch.*, 1918, **19**, 410—414).—In continuation of work previously published (A., 1915, ii, 673), further constants of

mercury are now given. All experiments were carried out in capillaries of quartz. A series of density determinations of liquid and gaseous mercury have been made at a series of temperatures, and the following values obtained : mercury vapour, D 0·7 at 1050°, 1·15 at 1210°, 1·35 at 1230°, 1·65 at 1295°, 1·90 at 1330°, and 2·50 at 1380°. These results imply that the critical temperature is above 1370°, a value considerably higher than that accepted by previous observers. As a first approximation, the value 200 atms. is given as the lower limit of the critical pressure. The density of liquid mercury has been determined at high temperatures, and the following figures obtained : 500°, D 12·38; 600°, D 12·10; 800°, D 11·49; 900°, D 11·11; 1000°, D 10·67; 1100°, D 10·18; 1200° D 9·57; 1300°, D 8·90. The emission of light of mercury has been examined; at 1270° the vapour emits no visible light, whilst the liquid emits a dazzling white light. Above 1270° the vapour space appears to be filled with weak blue light. From determinations of the light emission, it is shown that the temperature of mercury vapour can be fairly accurately determined. The results given in this last section of the paper are of a preliminary nature.

J. F. S.

Adsorption of Gases on Plane Surfaces of Glass, Mica, and Platinum. IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1918, **40**, 1361—1403. Compare A., 1917, ii, 19, 525).—The theory put forward previously (*loc. cit.*) is elaborated and discussed ; it is shown that the theory demands that in typical cases of true adsorption the adsorbed film should not exceed one molecule in thickness. This is contrary to the usual view, and the discrepancy is accounted for by the fact that in most cases porous bodies in which the adsorbing surface is indeterminate have been used in the experiments, or saturated vapours have been used, so that condensation of liquid took place in capillary spaces; also solution and absorption have been mistaken for adsorption. The mechanism of adsorption is discussed, and it is shown that the forces causing adsorption are typically chemical and exhibit all the differences in intensity characteristic of chemical forces. The adsorption of the permanent gases by solids involves only secondary valencies, but a great many cases of adsorption by metals are caused by primary valencies. Under certain conditions, stoicheiometric relations should govern the amounts of gases adsorbed on saturated surfaces. These relationships often fail to hold, because of steric hindrance effects between the adsorbed molecules. Equations are developed which give the relation between the amount of adsorbed gas and the pressure and other variables under various conditions. A number of experiments are described in which the amount of adsorption of nitrogen, methane, carbon monoxide, argon, oxygen, carbon dioxide, and hydrogen on surfaces of glass, mica, and platinum has been determined at various temperatures and low pressures (circa 0·1 mm. of mercury). At the ordinary temperature,

the adsorption by mica and glass was negligible, less than 1% of the surface being covered by a single layer of molecules. At $-183°$ and $-118°$, relatively large amounts of gases were adsorbed, except in the case of hydrogen, and at higher pressures the surfaces tended to become saturated with the gas. The maximum quantities adsorbed, even with saturated surfaces, were always somewhat less than the amounts expected from a unimolecular layer. The amounts of the different gases adsorbed by saturated surfaces of mica and glass were always in the order: hydrogen, oxygen, argon, nitrogen, carbon monoxide, methane, and carbon dioxide. The amounts adsorbed by mica and glass varied with pressure according to the equation $N/N_0 \times \eta = \theta_1 = \sigma_1\mu/(1 + \mu\sigma)$, in which N is the Avogadro constant $6·06 \times 10^{23}$ mols. per gram-mol., η is the number of gram-molecules of gas absorbed per unit area of surface, θ is the fraction of the surface actually covered by adsorbed molecules, μ is the number of molecules striking each cm. of surface per second, $\sigma = a/v_1$, where a is the fraction of the molecules which on striking the surface condense, and v_1 is the rate at which the gas would evaporate if the surface were entirely covered. The adsorption of all the above gases is reversible. The phenomena observed with platinum are quite different. No adsorption of gases could be observed, even at $-183°$, until the platinum had been activated by heating to $300°$ in a mixture of hydrogen and oxygen at low pressure. After this activation, hydrogen and oxygen, or carbon monoxide and oxygen, reacted together readily at the ordinary temperature in contact with the platinum. The platinum was then found capable of adsorbing oxygen, hydrogen, or carbon monoxide. The maximum quantities of oxygen and carbon monoxide corresponded with unimolecular layers. The oxygen could not be driven off either by heat or by exhaustion. When the platinum was in contact with an excess of oxygen, the amount of oxygen adsorbed increased as the temperature was raised, but was reversible. Adsorbed carbon monoxide could not be removed by exhaustion at the ordinary temperature, but at $300°$, part of it could be pumped off. When oxygen was brought into contact with carbon monoxide adsorbed on the platinum, it reacted rapidly to form carbon dioxide, which at the ordinary temperature showed no tendency to be adsorbed. In a similar way, carbon monoxide brought into contact with adsorbed oxygen reacted immediately. These cases of adsorption are clearly due to primary valencies.

J. F. S.

[**Chemical and Physical Theories of the Action of Toxins, Dyes, etc.**] P. KARRER (*Chem. Zeit.*, 1918, **42**, 521—522).— According to the physical theory (compare Traube, A., 1912, ii, 740), a toxin does not combine chemically with the substance (for example, albumin) on which it has an effect, but causes a precipitation or coagulation of the substance. The author is of opinion that the action is purely chemical; in the experiments

described by Traube, the minute quantity of precipitant employed was still more than was required to precipitate the substances as chemical compounds.   W. P. S.

Molecular Weights of Salts Dissolved in Urethane. G. BRUNI (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 321—323; *Gazzetta*, 1918, **48**, ii, 39—42).—Criticism of Stuckgold's results (this vol., ii, 99), some of which are erroneous and others inaccurately calculated; the literature of the subject has been disregarded.   For potassium iodide in urethane, Stuckgold's cryoscopic measurements gave values of 94 and 97 for the molecular weight, whereas the author finds values varying from 146·6 to 152·1, the mean being 150·2; the degree of dissociation is hence $a = 0·10$, and not 0·71—0·76.   T. H. P.

Osmotic Action of Solutions of Sucrose, Silver Nitrate, and Lithium Chloride in Pyridine, when separated from Pyridine by a Rubber Membrane. ALFRED E. KOENIG (*J. Physical Chem.*, 1918, **22**, 461—479).—Osmotic pressure determinations have been made of solutions of sucrose, silver nitrate, and lithium chloride in pyridine, using a modified form of cell and a thin sheet of dental rubber as membrane.   Solutions of concentrations from $0·2N$—$0·025N$ were used, and all measurements were made at 25°.   The osmotic pressure found for sucrose solutions was very near that demanded by the gas laws, but the values for silver nitrate and lithium chloride were much lower than those of sucrose of equal molecular concentration.   It was found that, after having reached a maximum, the osmotic pressure decreased.   This seemed to be due to an alteration in the nature of the rubber, due to its contact with pyridine, for membranes used a number of times with fresh solutions did not give as high a pressure as the unused rubber, whilst the same solution used several times with fresh rubber each time gave practically the same pressure in all measurements.   This the author takes to be a substantiation of the statement of Kahlenberg, that the osmotic pressure developed by a given solution depends on the nature of the semipermeable membrane.   J. F. S.

Inhibition in the Diffusion of Salts into Colloids. TETSUTARO TADOKORO (*J. Tokyo Chem. Soc.*, 1918, **39**, 61—73). —It has been observed that the diffusion of a mixed salt solution into a colloid, such as gelatin, egg-white, and the expressed juices of plants, through a semipermeable membrane is opposed by some inhibitory factor.   The mixed salt solutions, which can coagulate these colloids, show that they are subjected to a considerable hindrance during diffusion.   The cause of this phenomenon is considered to be as follows: a new membrane is formed at the surface of the colloid by the salts after they have diffused through the semipermeable membrane; this new membrane then retards the further diffusion of the salts.   J. F. S.

Ionic Theory of Solid Substances. A. L. BERNOULLI
(*Helv. Chim. Acta*, 1918, **1**, 289—296).—A theoretical paper
in which it is shown that the ion frequencies of solid substances
may be calculated from the volume elasticity, compressibility, and
wave-length of the absorption bands at low temperatures.

J. F. S.

The Development of Crystals. RENÉ MARCELIN (*Ann.
Physique*, 1918, [ix], **10**, 185—188).—A microscopic study of the
crystallisation of *p*-toluidine shows that the crystals develop, not
at the base, but at the surface by successive depositions.   The
layers of material which are deposited maintain a perfectly uniform
thickness, which may be as small as three molecular diameters.
Similarly, when a crystal dissolves, the change goes on at the
surface, the material disappearing by successive layers, each layer
maintaining a constant thickness, and it is found that the material
has a crystalline structure at a thickness of only twenty molecular
diameters.   W. G.

Theory of Gel Structure. W. A. OSBORNE (*Proc. Roy. Soc.,
Victoria*, 1918, [N.S.]. **30**, 153—158; from *Physiol. Abstr.*, 1918,
3, 308).—The author discusses the question as to whether the more
solid phase in a gelatin jelly has a crystalline structure or is truly
amorphous, and describes experiments on the shape of bubbles and
on fracture, which, without being conclusive, indicate lack of
sectorial character.   Some experiments on the Struve-Baumstark
phenomenon with gelatin gels are also described.   This phenomenon
concerns the extrusion of water from tissues, soaps, etc., on treat-
ment with ether.   A 2% gelatin jelly on immersion in ether
extrudes water, but a 5% set jelly does not.   The weaker jelly is
supposed by the author to hold part of the more liquid phase by
capillarity in the lattice of the more solid phase, whereas in the
stronger jelly the water exists in solid solution in the substance of
the framework.   H. W. B.

Structure of Gels. W. BACHMANN (*Kolloid Zeitsch.*, 1918, **23**,
85—100).—After a fairly long historical introduction on the struc-
ture of gels, the author describes a series of experiments on the
vapour pressure isothermals, the ultramicroscopic character, and
the capillary radii of the gels of gelatin in alcohol and benzene.
It is shown that these gels, apart from minor points, which affect
the general character but little, and are based on the mechanical
properties, present a far-reaching similarity in respect of the course
and hysteresis cycles of their vapour pressure isothermals with the
gels of silicic acid and other substances.   The isothermals are in
all cases built on a common type, which is approximately repre-
sented by the silicic acid gel in water.   This similarity points to a
common cause as the reason for the processes which obviously take
place in the same way, namely, lowering of the vapour pressure of
the imbibition liquid by the action of capillarity in an amicro-

scopic capillary system. Such a similarity in behaviour during the filling with liquid and emptying can be foreseen from Zsigmondy's theory for all porous substances with fine capillaries and resisting walls if secondary chemical processes are ruled out. This theory points to the structure of gels being that of a mass interspersed by a large number of fine capillaries. This type of hysteresis cycle must, if the theory is correct, be independent of the inhibition liquid and also of the gel material. These demands are amply confirmed by the experimental results. The application of the capillary theory to hardened gelatin gels allows of an approximate calculation being made of the volume of the capillaries. As a mean, it is shown that they are thirty to one hundred times smaller than the value put forward by Bütschli. It is also shown that capillaries of the size indicated by Bütschli (700—800 $\mu\mu$) can have no effect in the lowering of the vapour pressure.   J. F. S.

Esterification in Aqueous Solution. ATTILIO PURGOTTI (*Gazzetta*, 1918, **48**, ii, 54—62).—Experiments with alcohol and acetic acid show that in aqueous solution only slight esterification takes place, equilibrium being reached when about 1·2% of acetic acid is converted into the acetate. Sodium chloride increases this proportion to 7% and hydrochloric or sulphuric acid to about 19%. The catalytic effect of both organic and inorganic acids on this reaction is in proportion to their degree of dissociation. Gallic and tannic acids, however, retard the esterification. Phenols also exhibit catalytic action on the reaction, picric acid being the most effective, *m*-, *o*-, and *p*-cresols then following in order. Dihydric phenols are less active catalysts than the monohydric, whilst the trihydric ones behave like gallic and tannic acids.   T. H. P.

Velocity of Hydrolysis of Esters of the Types OR·[CH₂]ₙ·CO₂R′, OR·[CH₂]ₙ·O·CO′·R, etc. M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1914, [A], **5**, No. 4, 1—23; from *Chem. Zentr.*, 1918, i, 1143—1144. Compare A., 1914, i, 136).—In connexion with the earlier investigations on the influence of the position of the oxygen atom in the chain on the velocity of hydrolysis of esters, the author has now determined the velocities of hydrolysis of the same series of substances in alkaline solution at 15°. The reaction appears to be bimolecular, and a table of constants is given in the original.

The velocity constants for alkaline solution are approximately parallel to the dissociation constants of the corresponding acids. A minimum velocity, as in the case of acid hydrolysis, is not observed. The molecular weight has little influence on the constants.   H. W.

Influence of Temperature and Constitution on the Velocity of Hydrolysis of Esters by Hydrogen [Ion] Catalysis. FRIEDRICH BÜRKI (*Helv. Chim. Acta*, 1918, **1**, 231—250).— A large number of experiments have been carried out on the

hydrolysis of esters to ascertain (1) the influence of various acids, (2) the influence of concentration of the acid, (3) the influence of the constitution of the ester, and (4) the influence of temperature on the velocity of hydrolysis. The catalytic action of hydrochloric acid, nitric acid, sulphuric acid, and phosphoric acid of various concentrations on the hydrolysis of ethyl acetate has been determined at 25°, 30°, and 40°. The hydrolysis of the following esters by $0.1N$-hydrochloric acid at 40° has been quantitatively determined: methyl propionate, methyl n-butyrate, methyl α-chloropropionate, methyl α-dichloropropionate, allyl acetate, methyl crotonate, methyl isocrotonate, ethyl malonate, ethyl oxalate, ethyl acetoacetate, and isoamyl formate. It is shown that the relative velocity of hydrolysis by means of hydrogen ions is the same for all esters over the range 25—40°. Quantitative measurements could not be carried out in the case of acetoacetic ester, for the free acid undergoes the ketone decomposition at 40°. The catalytic action of the acids examined increases rapidly with increasing temperature. The increase is greatest with hydrochloric acid, somewhat smaller with nitric acid, and least with sulphuric acid. With a given concentration and temperature, the reaction proceeds most rapidly with nitric acid, somewhat less rapidly with hydrochloric acid, and most slowly with sulphuric acid. The influence of the substitution of one chlorine atom in the acid of the ester produced in the only case examined, that of α-chloropropionic ester, a lowering in the velocity of hydrolysis of about two-thirds the value of the unsubstituted ester. The introduction of two chlorine atoms brings the value up again to about five-sixths of the original value. The introduction of an unsaturated group into the alcohol produced no effect on the velocity of hydrolysis, whereas an unsaturated group in the acid greatly diminishes the velocity. The velocity constants multiplied by 10^6 are as follows at 40°: ethyl acetate, 5629; allyl acetate, 4642; methyl propionate, 6138; methyl α-chloropropionate, 2194; methyl α-dichloropropionate, 5281; methyl butyrate, 3462; methyl crotonate, 221; methyl isocrotonate, 985; ethyl malonate, 1158; isoamyl formate, 10,408.   J. F. S.

Dissociation Constants of Normal Acids and Esters of the Oxalic Acid Series. III. Effect of the Substitution of a Methylene Group by Bivalent Atoms and Radicles. M. H. PALOMAA (*Ann. Acad. Sci. Fennicae*, 1917, [*A*], **10**, No. 16, 1—26; from *Chem. Zentr.*, 1918, i, 1144. Compare A., 1913, i, 8).—Previous investigations have shown that the replacement of a methylene group in organic acids and esters by :O or :CO increases certain affinity constants in the homologous series (electrolytic dissociation constant, velocity of hydrolysis by alkali) and diminishes certain others, and that a minimum occurs with a certain position of the oxygen atom (velocity of hydrolysis by acid, velocity of esterification). The affinity minimum occurs when the oxygen is in the β-position or in the position 1:4—5. The result

is explained by supposing that intramolecular ring formation occurs through the medium of the partial valency of the oxygen. This hypothesis has been tested with the methyl esters of the oxalic acid series, which were dissolved in 50% methyl alcohol and hydrolysed with 0·05 mol. hydrochloric acid at 25°. Since the reaction leads to an equilibrium, the velocity of hydrolysis, as well as that of esterification, was determined. The results are expressed in tables. The minimum occurs with compounds in which the formation of a 5- or 6-membered ring is possible, as is demanded by the hypothesis.   H. W.

Neutral Salt Catalysis. I. Rôle of the Solvent in Neutral Salt Catalysis in Aqueous Solutions. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1918, **40**, 1461—1481).—A number of experiments on the accelerating effects of the chlorides of lithium, sodium, and potassium, in varying concentrations, on the iodine ion catalysis of hydrogen peroxide and on the hydrogen ion catalysis of methyl acetate are described. It is shown that the effects of the different salts are roughly proportional to their ionic hydration values as determined by Washburn. This is also shown to be the case in the hydrochloric acid catalysis of acetochloroanilide. In some cases, the effects of different salts on the velocity of hydrolysis of ethyl acetate are not proportional to the ionic hydration values, and reasons have been advanced to explain this abnormality. The chlorine ion activities up to a concentration $3N$ have been determined by measurement of cells of the type $Hg \mid HgCl \mid$ $NaCl(0·1N) \| NaCl(c) \mid HgCl \mid Hg$. The relationship $K_1/K_2 = a_1/a_2$ holds rigorously, where K_1 and K_2 are the velocity constants of the decomposition of hydrogen peroxide in the presence of potassium iodide and potassium chloride, and potassium iodide–sodium chloride solutions, respectively, both being of the same normality, and a_1 and a_2 are the chlorine ion activities of the potassium chloride and sodium chloride respectively. Relationships are expressed between the hydration values of the ions of neutral salts on the reaction velocities in neutral solutions, and also on the activities of salt solutions.   J. F. S.

The Atom Model. WILH. H. WESTPHAL. (*Ber. deut. physikal Ges.*, 1918, **20**, 88—92).—Polemical. In a short theoretical paper the author contests the objections to the Bohr atom model raised by Stark (this vol., ii, 141).   J. F. S.

Elements in Order of their Atomic Weights. RAYMOND SZYMANOWITZ (*Chem. News*, 1918, **117**, 339—340).—It is found that if the elements are written down in order of their atomic weights, a definite numerical sequence is to be observed in the values of the atomic weights. Thus, if the first element has an atomic weight of x, the second will be $x + 3$, the third $x + 3 + 1$, the fourth $x + 3 + 1 + 3$, and so on, adding alternately 3 and 1 to the preceding values. Of the 83 elements, 17 do not fall into

this arrangement, whilst there are several gaps with no known element to fill them.   It is pointed out that several of the elements which do not conform with the arrangement are little known rare elements, and that until 1918 these elements had atomic weights attributed to them which conformed with the present scheme.

J. F. S.

Elements in Order of their Atomic Weights.   F. H. LORING (*Chem. News*, 1918, **117**, 352).—The author points out that regularities of the type put forward by Szymanowitz (preceding abstract) have already been indicated, notably by Comstock (A., 1908, ii, 477).   J. F. S.

Interfacial Tension and Complex Molecules.   G. N. ANTONOFF (*Phil. Mag.*, 1918, [vi], **36**, 377—396).—A theoretical paper in which, from the modern conceptions of atoms and molecules, a theory of molecular attraction has been developed.   This theory implies that molecular attraction depends on the same forces as chemical affinity.   A relationship between surface tension and molecular pressure has also been deduced.   The interfacial tension a_{12} between two liquids is equal to the difference of the surface tensions against air $(a_1 - a_2)$ of both superposed liquid layers in equilibrium.   This result is in agreement with experimental values.   Two superposed liquid layers in equilibrium are to be regarded as solutions in the same solvent, and must contain an equal number of molecules per unit volume.   The so-called univariant systems may be obtained without fulfilment of the requirements of the phase rule if the molecules of the added component combine with those in solution without increasing their number.   J. F. S.

Theobald van Hogelende.   F. M. JAEGER (*Chem. Weekblad*, 1918, **15**, 1216—1258).—An account of the life and work of the alchemist Theobald van Hogelande, who was born at Middleburg about 1560, studied at Leyden in 1580, and at Paris in 1581. Most of his life was spent abroad, but he died in 1608, probably at Leyden.   A. J. W.

Isaac of Holland and Jan Isaac of Holland.   W. P. JORISSEN (*Chem. Weekblad*, 1918, **15**, 1343—1351).—A further contribution to the history of these alchemists (compare A., 1917, ii, 198, 461, 529).   A. J. W.

Simplification of some well-known Chemical Experiments.   S. GENELIN (*Zeitsch. physikal Chem. Unterr.*, **31**, 91—93; from *Chem. Zentr.*, 1918, ii, 250).—(1) *Reduction of Nitric to Nitrous Acid.*—Nitric acid (D 1·4, 0·5 c.c.) is mixed with water (500 c.c.) in two cylinders; after addition of potassium iodide– starch solution to each, a wad of zinc wool is dipped into one of the solutions.   Blue streaks are formed in a few seconds.

(2) *Oxidation of Ammonia to Ammonium Nitrite in the Air.*— Ten c.c. of concentrated ammonia solution are placed in a 2-litre flask, which is shaken for about a minute; the flask is placed horizontally, and a glowing piece of platinum foil is introduced. The platinum continues to glow, and brown fumes of nitrogen peroxide appear, which are replaced by a dense fog of ammonium nitrite. When the fog has subsided, the flask may be filled with water and the presence of the nitrite demonstrated by addition of sulphuric acid followed by potassium iodide and starch. (3) *Oxidation of Sulphur Dioxide to Sulphur Trioxide in Air.*— The experiment is performed in exactly the same manner as that just described, but with the replacement of ammonia by a solution of sulphur dioxide. (4) *Lead has a bright surface when it remains quite free from lead oxide.*—Molten lead is poured into a glass tube, the lower end of which is sealed, whilst the upper end is expanded to form a funnel; the tube is subsequently sealed.

H. W.

Experiments to Demonstrate the Velocity of Explosion of Mercury Fulminate. M. MITTAG (*Zeitsch. physikal Chem. Unterr.*, **31**, 93—95; from *Chem. Zentr.*, 1918, ii, 250).— About 20—30 mg. of mercury fulminate are placed in an empty percussion cap resting with open end upwards on a piece of foil at least 4 mm. thick; the foil is heated with the full flame of a Teclu burner. Explosion follows in ten to thirty seconds. The approximate duration of the flame can be shown by allowing it to illuminate a disk divided into forty-eight equal sectors, coloured alternately black and white; the disk is kept in rapid rotation (about 1500 revolutions per minute) by a small motor. Since the disk appears stationary, the duration of the explosion must be considerably shorter than 1/1200 second. Repetition with a disk containing ninety-six sectors shows the duration to be somewhat shorter than 1/2400 second.   H. W.

Inorganic Chemistry.

Two Sets of Distillation Apparatus for the Preparation of Large Quantities of Chemically Pure Acids in the Laboratory. E. KRUMMENACHER (*Schweiz. Chem. Zeit.*, 1917, **1**, 116—120; from *Chem. Zentr.*, 1918, ii, 1).—Detailed descriptions are given of apparatus for the preparation of hydrochloric acid on the counter-current principle, and for the distillation of nitric acid in a vacuum.   H. W.

Reduction in the Strength of Hypochlorite Solutions on Keeping. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1318—1324).—Under the influence of light, hypochlorite solutions

decompose rapidly, with formation of chlorate. In absence of light, solutions of moderately strong alkaline reaction keep for two months without much change (compare Bouvet, this vol., ii, 397). A. J. W.

Limit and Composition of the Terrestrial Atmosphere. Aurora Borealis ,Aerolites, and Shooting Stars. A. VÉRONNET (*Compt. rend.*, 1918, **167**, 636—638).—A theoretical discussion of the composition of the terrestrial atmosphere at heights varying from 0—300 km. The percentage of nitrogen increases regularly up to 100 km., and at a height of 100—150 km., nitrogen forms 0·96 of the atmosphere at a pressure less than $1·10^{-6}$ atmos., this being the region of auroræ boreales. The phenomena of aerolites and shooting stars are also discussed. W. G.

Simple Method for the Preparation of Phosphorous Acid. T. MILOBENDZKI and M. FRIEDMAN (*Chemik Polski*, 1917, **15**, 76—79; from *Chem. Zentr.*, 1918, i, 993).—Phosphorus trichloride is conveniently prepared by leading a current of chlorine through a layer of boiling phosphorus trichloride which covers a quantity of red phosphorus. The gas should not be introduced until the trichloride actually boils. The product thus obtained is pure and has b. p. 75·5°/749 mm. Formation of phosphorus pentachloride is not observed even after complete consumption of phosphorus. The production may be made continuous by distilling off the phosphorus trichloride and introducing the requisite quantity of phosphorus.

The violent reaction in the preparation of phosphorous acid from phosphorus trichloride may be avoided by effecting the decomposition of the latter with concentrated hydrochloric acid instead of with water; in the first instant, a slight rise in temperature is noted, but reaction proceeds subsequently at the ordinary temperature. Concentrated hydrochloric acid has the further advantage that it forms two layers with phosphorus trichloride, so that only a portion of the latter reacts at any given instant. H. W.

Behaviour of Phosphates at the Anode. FR. FICHTER and JAKOB MÜLLER (*Helv. Chim. Acta*, 1918, **1**, 297—305).—By the anodic oxidation of a solution of potassium monohydrogen orthophosphate $(2M)$ between two platinum electrodes in an undivided cell and in the presence of $2N$-potassium fluoride and 0·32 gram of potassium chromate per litre, the authors have prepared the potassium salts of monoperphosphoric acid (K_3PO_5) and perphosphoric acid $(K_4P_2O_8)$. The best yield is obtained at 5° and when working with a current density of 0·01 ampere per sq. cm. These salts have previously been prepared by Schmidlin and Massini (A., 1910, ii, 490), who obtained the acids by the action of concentrated hydrogen peroxide on phosphoric oxide, but failed to obtain the salts by the above method. The properties of the substances obtained are identical with those described by Schmidlin and Massini. J. F. S.

Preparation of Hypophosphates. R. G. VAN NAME and WILBERT J. HUFF (*Amer. J. Sci.*, 1918, [iv], **46**, 587—590).— After a recapitulation of the methods available for the production of hypophosphates, the authors describe a method which requires little attention in carrying out. A number of sticks of phosphorus are cast round glass rods, and these are supported from a plaster cover in a stout glass vessel containing about a litre of water and 250 grams of sodium carbonate, which need not be dissolved. The phosphorus sticks used were 9 c.m. long and 1·7 c.m. in diameter, and protruded about 1 c.m. from the solution. The whole is then put in a cool place and left to react. At the end of two or three days, some of the solution is withdrawn and tested with Congo-red to find the end of the reaction, which is reached when the turning point of the Congo-red is obtained. The phosphorus is then removed and placed in a similar solution. The product, sodium hydrogen hypophosphate, is found in part as a crystalline precipitate at the bottom of the jar, whilst the residue is obtained by concentrating the solution. It is crystallised to remove the accompanying phosphates and phosphites. The best temperature to carry out the reaction is 10—15°, and the yield is 10—16% of that theoretically possible.

J. F. S.

The Compound $H_2B_4O_6$ and its Salts. RAMES CHANDRA RAY (T., 1918, **113**, 803—808).—It has previously been shown (compare T., 1914, **105**, 2162) that the so-called amorphous boron, prepared by the reduction of boron trioxide by means of magnesium, probably consists of a solid solution of a lower oxide of boron, sometimes in combination with a little magnesium oxide, in elementary boron. The author has now extracted the fusion thus obtained with water, removed the boric acid from the solution by the method of Travers, Ray, and Gupta, and determined the ratios B/Mg and $B_2O_3/$(residue less MgO) in the resulting filtrate. The former ratio is found to be very nearly 4 and the latter 1·124, which closely approximates to the value of the ratio $2B_2O_3/B_4O_5$, which is 1·129. It is concluded that the filtrate contains a magnesium borite, the formula of which may be written MgO,B_4O_5, and this is confirmed by molecular weight determinations by the freezing-point method. The *potassium* salt, $K_2B_4O_6$, has been isolated by precipitating a solution of the magnesium salt with potassium hydroxide in equivalent proportions, and the formula confirmed by analysis and cryoscopic determinations. The constitutional formula of the corresponding acid is considered to be $BO(OH):BO\cdot BO:BO(OH)$, that of the oxide, B_4O_5, being

$$\begin{matrix} BO:BO \\ | \quad\quad >O. \\ BO:BO \end{matrix}$$

T. S. P.

Silicic Acid Gels. HARRY N. HOLMES (*J. Physical Chem.*, 1918, **22**, 510—519).—Methods for preparing silicic acid gels from water-glass by means of phosphoric, citric, acetic, formic, tartaric,

sulphuric, hydrochloric, lactic, trichloroacetic, monochloroacetic, and nitric acids are described. The concentrations and quantities of the various acids necessary to produce a gel which will set in a definite time have also been determined. The influence of temperature on the gels has been studied over the range 0—100°. It is shown that gels containing a very slight excess of hydroxyl ions set most rapidly, almost immediately if not too dilute, but with increase of hydrogen ion concentration the time required to set increases rapidly. With each acid there is a definite concentration of hydrogen ion which delays the setting indefinitely. At still higher concentrations of the same acid, the time required again becomes measurable and rapidly decreases to an almost instantaneous setting. Contrary to Flemming (A., 1902, ii, 646), it is shown that, in addition to the concentration of silicic acid, temperature, and catalytic action of the ions, the dehydrating influence of the non-ionised molecules also exerts a marked action on the time required for setting. J. F. S.

The Dissociation of Salt. H. V. Thompson (*Trans. Ceramic Soc.*, 1918, **17**, (2), 340—350).—Salt was heated for six hours in a platinum tube in a current of dry or moist air at a temperature of 110°, and the amount of salt vaporised and redeposited in a cool part of the tube was weighed. With dry air, the amount of salt volatilised was about 0·055 gram per litre, but with air saturated with moisture it rose to 0·08 gram per litre, an increase of 40%, due to the hydrolysis of the salt by the water. In order to investigate the effect of salt and water vapour on certain substances, these were placed in a platinum tray and inserted in the apparatus. Selected chips of quartz were rendered opaque and the sharp edges and rough surfaces were smoothed by the mixed vapour, a compound corresponding with $Na_2O:1·023SiO_2$ being formed superficially. In dry air, the quartz was much less attacked. Commercial ferric oxide was converted into magnetic iron oxide and numerous black, shining crystals in the presence of salt and water vapour at 1100°. The black crystals of magnetic iron oxide were also formed when ferric oxide was mixed with an excess of salt and heated for twelve hours in the full blast of a Teclu burner. The crystals appear to be due to the presence of salt, as they are not formed when ferric oxide is heated alone. Alumina on similar treatment became coated with a layer of fused material, which may be a sodium aluminate, $2Al_2O_3,9Na_2O$. In clays, a more deeply seated action occurs. A. B. S.

The System Lime–Alumina–Silica and its Relation to Slags and Portland Cement. B. Neumann (*Stahl u. Eisen*, 1918, **38**, 953—960).—The author summarises the results of various investigations on the binary and ternary systems of lime, alumina, and silica, and points out that the possible compositions of slags and Portland cements only occupy very small areas in the triangular diagram used to represent such ternary mixtures. He

refers to J. E. Johnson, jun.'s (*Met. and Chem. Eng.*, 1916, 363), curve showing the composition–temperature relations for freely flowing slags and its general identity with mixtures of the pure oxides of the same compositions, and suggests that a further study of such mixtures may have far-reaching consequences

Mixtures corresponding with Portland cements occupy an extremely small area in the triangular diagram, and the position of this area renders untenable the various theories which are based on the existence of a ternary compound in Portland cements. The author accepts Rankin's suggestion (*J. Franklin Inst.*, 1916, 181) that Portland cement is produced by the formation of the compounds $2CaO,SiO_2$ and $5CaO,3Al_2O_3$, which absorb lime and form tricalcium silicate and tricalcium aluminate. The former is regarded as the essential constituent of the cement, the latter acting chiefly as a flux or solvent which reduces the temperature at which the former is produced. Further investigations with a view to discover other solvents, together with a study of the effect of replacing alumina by iron oxide, are suggested. [See also *J. Soc. Chem. Ind.*, December, 1918.]   A. B. S.

The Carbides of the Rare Earths of the Cerium Group. A. DAMIENS (*Ann. Chim.*, 1918, [ix], **10**, 137—183).—A study of the action of water on the carbides of cerium, lanthanum, neodymium, praseodymium, and samarium. The gas evolved in every case consisted of a mixture of hydrogen, saturated hydrocarbons, ethylenic and acetylenic hydrocarbons. The proportion of hydrogen was in all cases high. In no case was any methane found, the saturated hydrocarbons consisting of ethane, propane, and *iso*butane. The ethylenic hydrocarbons consisted of ethylene and its homologues, and the acetylenic hydrocarbons of acetylene and its homologues. The different constituents of the mixture were invariably present, but their relative proportions varied according to the velocity of the reaction, which was dependent on the physical state of the carbide.

The metallic hydroxides produced were always those of the sesquioxides. *Cerous hydroxide* was isolated as a white substance, which fixes oxygen in the cold with the development of heat and the formation of ceric hydroxide.   W. G.

Gallium. L. M. DENIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—See this vol., ii, 456.

The Heterogeneity of Steel. H. LE CHATELIER and B. BOGITCH (*Compt. rend.*, 1918, **167**, 472—477).—The macrographic etching of steel shows a heterogeneous structure which is unaltered by heat treatment, as distinguished from the micrographic etching. Macrographic heterogeneity is due to oxygen in solid solution in the metal, and phosphorus or sulphur has no direct influence. The difference in the value of the electrical resistivity of steel as calculated from the chemical composition (excluding oxygen) and

as actually determined is considered to be due to the presence of oxygen in the steel. [See, further, *J. Soc. Chem. Ind.*, 701A.]

A. K.

The Metallographic Examination of Tinplate. L. MAYER (*Stahl u. Eisen*, 1918, **38**, 960—962).—It is commonly thought that the adhesion of tin to iron in tin-plate is due to the formation of a compound of the two metals. The author has examined pieces of commercial tin-plate with negative results. He immersed small cubes of iron of high and low carbon content in tin at various temperatures, and on examining these under the microscope found a layer of intermediate crystals, the thickness of the layer varying with the temperature of immersion. At 500°, part of the pearlite in the high carbon iron and at 750° that in the low carbon iron disappeared, but reappeared around the edges of the tin at 950°. From this, the author concludes that the diffusion of tin and iron at various temperatures may be indirectly traced by the behaviour of the pearlite and ferrite forms of iron at high temperatures. [See also *J. Soc. Chem. Ind.*, 736A.]

A. B. S.

Formation of Iron Disulphide by Wet Methods. V. RODT (*Mitt. K. Materialprüf.*, 1918, **36**, 93—107).—The first product of the action of hydrogen sulphide on iron hydroxide is iron trisulphide; if the reaction is carried out at a higher temperature, this is decomposed with the formation of iron disulphide, FeS_2, which is insoluble in hydrochloric acid. As thus obtained, iron disulphide has D_4^{18} 4·588, which is nearer to that of marcasite (4·55 to 4·88) than to that of pyrites (4·9—5·2). The reaction, $Fe_2S_3 \longrightarrow FeS_2 + FeS$, does not take place in the presence of substances having an alkaline reaction. Iron disulphide may also be obtained by boiling freshly prepared iron monosulphide, suspended in water, with sulphur in the absence of alkaline substances. These reactions would account for the formation of iron disulphide in soils containing iron hydroxide compounds and putrescent matter and free from alkaline earth carbonates. [See also *J. Soc. Chem. Ind.*, 732A.]

C. A. M.

Crystal Structure of Grey Tin. A. J. BIJL and N. H. KOLKMEYER (*Chem. Weekblad*, 1918, **15**, 1264).—Grey tin has a crystalline structure, the crystals belonging to the cubic system. The tin atoms are arranged similarly to the carbon atoms in diamond.

A. J. W.

Galvanic Potential of Alloys. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 345—372; from *Chem. Zentr.*, 1918, ii, 265—267).—Mixed crystals show resistance limits towards galvanic polarisation as well as towards chemical reagents (A., 1917, ii, 448). It was desirable to investigate the connexion between the potential of alloys and their composition, since the thermodynamic theory denies the possibility of the existence of galvanic resistance limits.

According to this theory, the metallic phase is in equilibrium with the electrolyte, so that even in the metallic phase the change of position of the two kinds of atoms is sufficiently frequent for the establishment of a definite concentration. This condition is not fulfilled at temperatures at which chemical resistance limits occur. The thermodynamic theory is developed for a homogeneous binary metallic mixture, and a number of the conclusions are experimentally verified. Silver–gold mixed crystals were investigated with the electrometer, using the system $Ag | 0.02AgNO_3 | 0.1KNO_3 | 0.01AuCl_3 | Au$; the potential of the open system is definite. When the silver electrode is replaced by alloys of silver and gold, the potential is found to depend on the previous history of the alloy; the results can be interpreted by assuming that Ag–Au atoms are unable to change places with one another. The Ag atoms are superficially removed by boiling nitric acid, and the surface behaves then as if composed of gold. If the surface is rubbed with emery, a portion of the superficial gold is removed and the silver atoms again come to the surface. The behaviour of plates with untouched surfaces after prolonged tempering is unexpected; the potential of silver is first exhibited, which rapidly decreases, approximates to the potential of gold, and finally, after eighteen hours, increases to that of silver. The potential at which noticeable polarisation occurs is, within the limits of error, the same for gold and for gold–silver alloys with more than 0.5 mol. Au; this is particularly marked for NO_3 anions. The gold content at which the polarisation potential decreases (0.5 mol. Au) is independent of the valency of the polarising anion, whilst with chemical agents it depends on the number of Ag atoms which react with a molecule of the reagent. With a gold content less than 0.5 mol., polarisation is greatly dependent on the treatment of the electrodes. The galvanic and chemical resistance limits for 0.5 mol. Au are identical for simple reagents. If the structure of a series of metallic conglomerates is unknown, no conclusion can be drawn from the relationship between the potential line and the composition as to whether the conglomerate consists of one or two types of crystals in those regions of concentration in which the potential is independent of the concentration, neither is the sudden alteration of potential with alteration of concentration a sign of the formation of a new type of crystal. Such conclusions are only justified when the atoms are sufficiently mobile, as is the case with Au–Ag alloys at 320°, when a continuous alteration of the potential with the concentration is observed. The work of other authors also shows that the potential of a series of mixed crystals alters continuously with the concentration when diffusion is sufficiently rapid, and that the potential of a series of alloys with two types of crystal is independent of the concentration (Cd amalgams); when, however, diffusion is not sufficiently rapid to keep the surface concentration definite, the potential is either independent of the concentration or alters very rapidly, the alteration beginning at a concentration corresponding with multiple pro-

portions. The galvanic limits are also those of the precipitation of other metals from their solution. The non-resistant and the relatively resistant mixed crystals are distinguished in their precipitating ability, since the former also precipitate those metals the potentials of which lie between the true values of the unchanged surface of the resistant and that of the relatively resistant mixed crystals. Thus, Ag–Zn mixed crystals with less than 0·25 mol. Ag precipitate all metals from zinc onwards, whilst those with more than 0·25 mol. Ag, the potential of ·which towards zinc is more than 0·6 volt, only precipitate lead and the following metals.

The resistance limits of Au–Ag mixed crystals are considered from the space lattice theory. The condition of the less noble metal in a series of mixed crystals can be deduced from the value of the potential at which it passes into solution. If it dissolves at its own potential, it is present in the free state and a second galvanic limit cannot occur (Cu–Au and Ag–Au mixed crystals), if it dissolves at a lower potential, it is present in the combined state, and a second resistance limit may be found (Zn–Au mixed crystals with 0·17—0·37 mol. Au, from which it follows that the crystals from 0·43—0·64 Au contain the compound AuZn). The difference between a mixed crystal and a chemical compound depends on the electrons surrounding the positive core.   H. W.

The Limits of the Gold Content within which Copper–Gold and Silver–Gold Mixed Crystals are attacked by Chemical Reagents. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 385—425; from *Chem. Zentr.*, 1918, ii, 268—270. Compare preceding abstract).—The resistance limits of the mixed crystals mentioned above have now been determined with greater accuracy than in the case of the previous investigation (A., 1917, ii, 448), and it is now possible, in the most favourable cases, to define these limits for differences of concentration as low as 0·001 mol. Au. The degree of accuracy depends chiefly on the distinctness of the alteration caused by the agent on the surface, and the separation of an opaque, slightly soluble product is advantageous. Accuracy is favoured by evenness and uniformity of surface. In the crystallisation of mixed crystals, it is general to find a difference between the compositions of the molten residue and of the crystals which causes lack of homogeneity in the conglomerate, so that the latter is not uniformly coloured by a chemical reagent. This defect can be greatly remedied by tempering, preferably at a high temperature, and also by rolling. The influence of the duration of tempering on the uniformity of the alloy was particularly investigated with an Ag–Au alloy containing 0·49—0·51 mol. Au; after ordinary cooling, in which the temperature interval 1000—300° was passed through in fifteen minutes, the alloy showed no particles in which the percentage of gold differed by more than 0·75% from the mean value; after tempering for four hours at 700°, differences of concentration equivalent to 0·005 mol. Au remained.

The action of palladium chloride solution (4%) on Cu–Au alloys with 0·23—0·27 mol. Au has been studied; the plates with natural surfaces precipitate palladium when containing less than 0·25 mol. Au, and this limit is easily perceived with a difference of less than 0·005 mol. Au. The action of palladium nitrate on Ag–Au alloys, and of platinous chloride on Cu–Au and Ag–Au alloys, is also described. Cu–Au mixed crystals with 0·282 Au and more remain untarnished for a year in yellow ammonium sulphide solution, whereas alloys with 0·243 and less Au are completely blackened after a few hours or days; in this respect, mixed solutions of ammonium sulphide and disulphide act most rapidly, followed in order by solution of sulphur in sodium sulphide, sodium sulphide solution, and solution of sulphur in carbon disulphide. The sequence of darkening, previous to tempering for twelve hours at 720°, did not correspond with the copper content; after such tempering, the tendency to darkening decreased regularly with increasing gold content. The action of sodium sulphide only occurs in presence of oxygen, whilst with polysulphide solutions this is unnecessary. The limit of deep-seated action of Na_2S_2 solution on Cu–Au crystals lies between 0·245 and 0·255 mol. Au; with polished plates, it is slightly more than 0·270 Au. The same solutions were used with Ag–Au mixed crystals; in this case, darkening with ammonium disulphide solution occurs far more regularly. Increase in the period of tempering diminishes the rapidity of the action. Sodium disulphide solution behaves similarly, but more rapidly. The previous datum, that mild oxidising agents, such as hydrogen peroxide, air, alkaline sodium tartrate, or picric acid, are active up to a gold content of 0·243 mol. cannot be fully maintained; the limit is now found at about 0·22 mol. For powerful oxidising agents, the following limits were observed: $AuCl_3$ (0·495—0·505 mol. Au); H_2CrO_4 (0·492); $HMnO_4$ (0·495—0·505); HNO_3 (0·480—0·490). Mercurous salts react with the complete series of Cu–Au alloys, but not with pure gold. The rate of action increases with the concentration of the solution, with which, also, the nature of the alteration of the plate varies. Alloys containing up to 0·24 mol. Au precipitate mercury from mercuric chloride solution, whilst those richer in gold precipitate mercurous chloride. Silver salts have a limit of 0·05—0·15 for Cu–Au alloys, but precipitation occurs at isolated spots, from which, with simple salts, needles or leaflets grow with visible rapidity. The limits vary with the nature of the negative ion, and vary considerably round a gold content of $\frac{1}{8}$ mol. The limits of precipitation with hard, untempered plates lie at a slightly higher gold content than for tempered plates. It is generally observed that the action of a reagent with distinct limits is noticeable after a few days, and does not then change after several months. The superficial nature of the alloy is of great importance for the action limits; the natural surface is the most resistant. If the alloy is rubbed with the finest emery paper, numerous scratches are formed at the surfaces, of which the usual distribution

of the atoms in the lattice is disturbed. The distribution of the atoms, caused by grinding and polishing, approximates to the unarranged, which is far less resistant than the normal distribution. In many cases, protective layers are formed during tempering, which can be recognised by the diminution of the time of attack with increasing period of tempering. The numerical values of the action limits are partly multiples of one-eighth within the limits of experimental error; at times these multiples are not quite attained, whilst at others they are noticeably exceeded.

The various reagents are classified with respect to action limits, and attempts are made to explain the actions of mixed crystals by means of lattice models.
H. W.

Behaviour of Mixed Crystals of Copper, Silver, and Gold towards Chemical Reagents and the Colour of these Mixed Crystals. G. TAMMANN (*Nachr. K. Ges. Wiss. Göttingen*, 1917, 373—384; from *Chem. Zentr.*, 1918, ii, 267—268. Compare preceding abstracts).—The problem of the resistance limits of ternary mixed crystals is of interest from the theoretical standpoint and also from the practical point of view of the possibility of the partial replacement of the noble metal of a binary resistant alloy with the formation of an equally resistant ternary mixture. The experiments described have been performed with Cu, Ag, Au alloys, since the resistance limits of the binary systems have been investigated. A series of mixed crystals has been prepared in which the atomic ratios Ag to Cu has been kept constant at $1:2$, $1:1$, and $2:1$, respectively, whilst the amounts of gold were increased by 0.05 mol. between 0.20 and 0.55 mol. In the case of the second of the series, the alloys were investigated in the hard and soft states, but, as no noticeable differences were observed, the remaining alloys were only used in the latter condition. In contrast to the author's experience with binary alloys (A., 1917, ii, 448), the resistance limits with ternary alloys are more or less indefinite, and it is necessary to distinguish between the limits of deep-seated and superficial action; the latter is commonly associated with a much higher gold content than the former, and this is particularly marked in the cases of the action of concentrated nitric acid and of a mixture of chromic and sulphuric acids. The action limits of the following reagents on the ternary alloys have been investigated: ammonium disulphide, palladium chloride and nitrate, picric acid, potassium dichromate and sulphuric acid, nitric acid, gold chloride, permanganic and sulphuric acids. In respect of deep-seated action, the ternary alloys are generally more noble than the binary.

A number of observations on the colour of ternary alloys are schematically recorded. The distribution of the different types of atoms in a 14-point lattice is also discussed.
H. W.

Mineralogical Chemistry.

Pyrolusite from Virginia. THOMAS L. WATSON and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1918, **8**, 550—560).—The manganese ore mined in Little Fork Valley, near Woodstock, in Shenandoah Co., occurs as an impregnation and replacement in brecciated sandstone and conglomerate in the trough of a syncline. It consists mainly of crystalline, fibrous pyrolusite with some wad. Small crystals are abundant, lining cavities. The colour is black, but steel-grey on fresh fractures, with metallic lustre; streak, black to slightly bluish-black. H. $2\frac{1}{2}$. Anal. I is of crystals and II of crystalline, fibrous material.

	MnO_2.	MnO.	Fe_2O_3.	Al_2O_3.	BaO.	CaO.	SiO_2.
I.	94·30	2·25	0·22	0·14	0·33	0·08	0·64
II.	95·22	1·31	0·17	0·18	0·40	0·11	0·63

	P_2O_5.	H_2O (> 105°).	H_2O (< 105°).	Total.	Sp. gr.
I.	0·52	1·53	0·22	100·23	4·748
II.	0·58	1·46	0·16	103·22	4·885

The material thus has the physical characters and composition (MnO_2) of pyrolusite, but, as usual, the crystals have the orthorhombic form and habit of manganite. The axial ratios, $a:b:c = 0.8616:1:0.5628$, however, differ somewhat from those usually accepted for manganite ($0.8441:1:0.5448$), although they are very close to the value for manganite from Böhlet, Sweden ($0.8612:1:0.5629$, G. Flink, 1900). It is thus just possible that these are original crystals of pyrolusite rather than pseudomorphs after manganite, as commonly believed.   L. J. S.

Deposits of Potassium Salts at Dallol (Eritrea). M. GIUA (*Atti R. Accad. Lincei*, 1918, [v], **27**, i, 331—335; *Gazzetta*, 1918, **48**, ii, 1—8).—The results are given of analyses of a number of samples from the salt deposits of Dallol, in S. Dancalia (Eritrea). At many points these deposits consist largely of potassium chloride (up to 98·6%), whilst at others sodium chloride predominates. In both cases, the proportions of magnesium chloride are low, and only traces of bromides are present in a few instances. The potassium minerals occur at the surface of the earth and are localised at certain points of the salt area. The thermal springs of Dallol have a temperature of about 80—90°, and consist of saturated solutions of magnesium chloride containing traces of sodium chloride and appreciable proportions of magnesium bromide.   T. H. P.

Etching of Gypsum by Concentrated Sulphuric Acid. ROMAN GRENGG (*Tsch. Min. Mitt.*, 1915, **33**, 201—226; from *Jahrb. Min.*, 1918, Ref. 135—136. Compare A., 1915, ii, 450).—Crystals of gypsum immersed in concentrated sulphuric acid

develop on the faces flat hillocks with a more or less elliptical out-line. This type of etch-figure is described as 'etch-shield,' as distinct from 'etch-hill.' The solution of the gypsum gives rise momentarily to a supersaturated solution of $CaH_6(SO_4)_4$, from which are deposited microscopic aggregates, probably the hemi-hydrate, $CaSO_4,\frac{1}{2}H_2O$. The process proceeds with the formation of mainly the monoclinic salt, $CaH_6(SO_4)_4$, together with the acid salt, $CaH_2(SO_4)_2$. After a time, the process becomes slower, and spaces corresponding with the 'etch-shields' appear in the cover-ing layer of acid calcium sulphate. At a later stage, the acid acts by extracting water from the gypsum, with the production of the characteristic weathering surfaces, until, finally, the whole crystal is transformed into anhydrous calcium sulphate. The 'etch-shields' approximate to the position of the plane (807), perpen-dicular to which is the greatest solubility in the concentrated acid.

L. J. S.

The Constitutional Formula of Nephelite. St. J. Thugutt (*Spraw. Tow. Nank. Warszaw.*, *Math.-naturw. Kl.*, 1913, **6**, 849—862; from *Jahrb. Min.*, 1918, Ref. 132—133).—The author defends the formula $8Na_2Al_2Si_3O_{10},4Na_2Al_2O_4,3K_2Al_2Si_3O_{10}$ pre-viously proposed by him (A., 1895, ii, 358), and criticises later views (A., 1911, ii, 122, 992; 1912, ii, 176, 569). Morozewic's formula, $K_4Na_{18}Al_{22}Si_{23}O_{90}$ (A., 1908, ii, 202), for 'basic' nephelite can be expressed as

$$18Na_2Al_2Si_3O_{10},9Na_2Al_2O_4,K_2Al_2O_4,5K_2Al_2Si_3O_{10}.$$
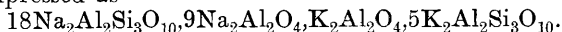
By the action of superheated water, nephelite splits up into natrolite ($Na_2Al_2Si_3O_{10},2H_2O$), gibbsite [$Al(OH)_3$], and muscovite [$H_2KAl_3(SiO_4)_3$], whilst some of the sodium goes into solution, these minerals corresponding in composition with the three mole-cules in the author's formula. It is suggested that the variations in analyses of nephelite may be due to want of homogeneity of the material, and that the secondary minerals mentioned above may be present in an extremely finely divided state. L. J. S.

Analytical Chemistry.

The Use of Thymolsulphophthalein as an Indicator in Acidimetric Titrations. ARTHUR B. CLARK and HERBERT A. LUBS (*J. Amer. Chem. Soc.*, 1918, **40**, 1443—1448. Compare A., 1916, ii, 44, 570).—Thymolsulphophthalein, an indicator having two useful working ranges, can be very successfully employed in many differential acidimetric and alkalimetric titrations. To illustrate the general method of employment, a few typical titrations are given (mixtures of benzoic and hydrochloric acids, acetic

and hydrochloric acids, acetic and sulphuric acids, titration of aniline by hydrochloric or sulphuric acid). Any acid with a dissociation equal to or weaker than that of acetic acid may be differentially titrated in the presence of hydrochloric acid, provided that the weaker acid is completely neutralised when the alkaline colour change of the indicator occurs.

The use of proper colour screens or, preferably, of a colorimeter or spectrophotometer, greatly increases the accuracy of differential titrations, but is not absolutely necessary.   H. W.

Titration of Free Hydrochloric Acid in Gastric Juice with Suppression of the Dissociation of Organic Acids by Addition of Alcohol. GEORG KELLING (*Berl. klin. Woch.*, 1918, **54**, 334—336; from *Chem. Zentr.*, 1918, i, 1063—1064).—The use of dimethylaminoazobenzene, Congo-red, or tropæolin for the detection of free hydrochloric acid is rendered uncertain by the presence of large amounts of organic acids or of loosely combined hydrochloric acid. The author recommends the following process, which, in a simple manner, gives results which are in close agreement with those obtained by Günzburg's method. Two drops of a 0·5% solution of dimethylaminoazobenzene in alcohol (90%) are added to 5 c.c. of gastric juice; an intense carmine-red coloration denotes the presence of free hydrochloric acid. 7·5 C.c. of alcohol (96%) are added, and the solution is titrated with $N/10$-potassium hydroxide until a pure yellow shade is obtained. (If more than 2·5 c.c. of alkali are required, it should be observed that the volume of added alcohol must be approximately half that of the aqueous liquid.) The acidity of 10 c.c. is calculated by multiplying by 2 and adding 3. The addition is necessary, since the alcohol affects the acidity of free hydrochloric acid for the indicator to this extent. When free hydrochloric acid is absent and the hydrochloric acid deficit is to be estimated, a similar process is adopted—an equal volume of alcohol is added, followed by hydrochloric acid, until a red coloration is produced; the solution is then titrated back with $N/10$-potassium hydroxide. The two acid values are subtracted, the difference is calculated to 10 c.c., and increased by three. The added alcohol completely suppresses the acidity of organic acids so far as the reaction is concerned.
                                                                    H. W.

Colorimetric Scale for the Estimation of Free Hydrochloric Acid [in Gastric Juice] by means of Brilliant-Green. M. DELORT and ROCHE (*Compt. rend. Soc. Biol.*, 1918, **81**, 646—649).—An unfiltered 1% solution of methylene-blue in dilute alcohol, a 5% aqueous solution of normal potassium chromate, and an unfiltered 0·1% solution of eosin in dilute alcohol are mixed with water in six given proportions. The mixtures are kept in sealed tubes, and constitute a permanent scale of colours which match those produced by mixing equal volumes of a 0·02% solution of brilliant-green with gastric juice containing six different concentrations of free hydrochloric acid (0·025% to 0·2%).   G. B.

I. Detection and Separation of Hydrochloric Acid in Presence of Bromic and Iodic Acids. II. Detection and Estimation of Bromic and Iodic Acids in Presence of Hydrochloric, Hydrobromic, and Hydriodic Acids. ATTILIO PURGOTTI (*Gazzetta*, 1918, **48**, ii, 63—66).—The methods here proposed are based on the fact that potassium or sodium hydroxide attacks silver bromate and iodate in the cold, whereas silver chloride, bromide, and iodide remain unchanged. [See *J. Soc. Chem. Ind.*, 730A.]   T. H. P.

Estimation of Hypochlorite and Chlorate in the same Mixture. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1289—1295).—The estimation of hypochlorite and chlorate in such a substance as bleaching powder is carried out as follows.

To 25 c.c. of $N/10$-arsenious oxide solution are added 5 c.c. of $4N$-acetic acid and three drops of 0.2% methyl-red. The hypochlorite solution is then run in until the liquid is decolorised, the number of c.c. used containing 88.75 mg. of active chlorine.

To the colourless solution thus obtained are added 25 c.c. of the arsenious oxide solution and 20 c.c. of concentrated hydrochloric acid, and the mixture boiled for five minutes. The excess of arsenious oxide is then estimated by titration with $N/10$-potassium bromate, each c.c. of arsenious oxide solution used corresponding with 1.4 mg. of ClO_3 or 3.45 mg. of active chlorine.   A. J. W.

Estimation of Sulphuric Acid and Barium as Barium Sulphate. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 212).—A reply to Karaoglanow (this vol., ii, 369).   W. P. S.

Volumetric Estimation of Sulphates. VANSTEENBERGER and BAUZIL (*Ann. Chim. anal.*, 1918, **23**, 210—214).—The solution containing a sulphate is heated at 60—70° with an excess of sodium carbonate solution, filtered, the filtrate slightly acidified with hydrochloric acid, and treated with an excess of standardised barium chloride solution. The mixture is boiled for one minute, filtered, and the excess of barium in the filtrate precipitated as barium carbonate, which is collected, washed, and titrated with $N/10$-hydrochloric acid, using methyl-orange as indicator. [See, further, *J. Soc. Chem. Ind.*, 689A.]   W. P. S.

Volumetric Estimation of Selenious Acid and Selenic Acid. L. MOSER and W. PRINZ (*Zeitsch. anal. Chem.*, 1918, **57**, 277—305).—The iodometric estimation of selenious acid is trustworthy if the selenious acid is heated in a distillation flask with four times the theoretical quantity of potassium iodide in the presence of hydrochloric acid, and the liberated iodine titrated in the receiver and in the residue. The indirect iodometric method described by Gooch and Pierce (A., 1896, ii, 334) is also trustworthy if carried out as a distillation process. Oxidation with permanganate in alkaline solution as proposed by Marino (A.,

21*

1910, ii, 155) is untrustworthy if the oxidation mixture is acidified before cooling. Titration of selenious acid with titanium trichloride solution does not give accurate results, owing to the formation of a quantity of hydrogen selenide. Reduction with hydriodic acid is the most trustworthy method for the estimation of selenic acid. [See, further, *J. Soc. Chem. Ind.*, 730A.]

W. P. S.

Estimation of Nitrogen in Urine by Kjeldahl's Method.

C. OEHME and M. OEHME (*Ber. Klin. Woch.*, 1918, **55**, 401—402 : from *Chem. Zentr.*, 1918, ii, 70).—To economise reagents, gas, and time, the authors recommend a reduction in the quantities usual for a Kjeldahl estimation, and propose the following process. Urine (1 c.c.) and concentrated sulphuric acid (2 c.c.) are heated in the usual manner after addition of potassium and copper sulphates. Distillation, after addition of water (100 c.c.) and sodium hydroxide solution (33%, 15—20 c.c.), is usually complete in fifteen to twenty minutes. $N/20$-Acid is conveniently used for titration.

H. W.

Estimation of the Residual Nitrogen in Blood-serum.

FISCHER (*Zeitsch. physiol. Chem.*, 1918, **102**, 266—274).—In the estimation of the residual nitrogen in blood-serum, it is essential that the proteins should be so completely removed by precipitation that no trace of the latter can be detected in the filtrate. This result can be achieved by precipitating with sodium acetate or chloride in the presence of acetic acid at 100°, or by treatment with uranium acetate at the ordinary temperature. The author recommends the uranium acetate method, which yields values for the residual nitrogen varying from 20 to 90 mg. of nitrogen per 100 c.c. of blood-serum.

H. W. B.

Estimation of Minimal Quantities of Nitrites and Hydrogen Peroxide, either Separate or Present together.

A. QUARTAROLI (*Gazzetta*, 1918, **48**, i, 102—111).—Less than one part of nitrite per million of water may be detected by the blood-red coloration given by a reagent containing potassium thiocyanate, ferrous sulphate, and nitric acid. The same reaction is given by hydrogen peroxide, potassium persulphate, and probably other peroxygenated compounds, but not by chlorates or perchlorates. With hydrogen peroxide, the coloration produced is less intense than that with nitrous acid, but the reaction is more sensitive than any other for the peroxide. With nitrous acid, but not with hydrogen peroxide, the coloration formed disappears when the solution is heated rapidly to boiling with concentrated hydrochloric acid and carbamide. [See *J. Soc. Chem. Ind.*, 731A.] T. H. P.

Methods for the Estimation of Phosphoric Acid in Small Amounts of Blood.

W. R. BLOOR (*J. Biol. Chem.*, 1918, **36**, 33—48).—The estimation of the phosphoric acid is based on its

precipitation as strychnine phosphomolybdate by a modification of Kober and Egerer's method (A., 1915, ii, 794). The amount of precipitate is estimated nephelometrically.   H. W. B.

Detection, Estimation, and Elimination of Arsenic and Mercury in Urine. PAUL DURET (*Compt. rend. Soc. Biol.*, 1918, **81**, 736—737, 737—739).—See this vol., i, 561.

Microchemical Notices. O. TUNMANN (*Pharm. Post.*, 1918, **51**, 341—342, 353—354; from *Chem. Zentr.*, 1918, ii, 401—402. Compare this vol., ii, 465).—II. *Occurrence of a Crystalline Substance in the Seeds of* Strychnos nux vomica, L.—In a single instance out of several hundred seeds examined, considerable quantities of colourless needles of chlorogenic acid were observed.

III. *Identification of Arsenious Acid.*—The extension of microchemical methods to chemical preparations is considered a hasty step by the author (contrast Wasicky and Mayrhofer, *Zeitsch. allg. Österr. Apoth. Ver.*, **55**, 305); the method should be restricted to drugs. Arsenious acid is best detected by sublimation from an asbestos plate at a comparatively high temperature; the method can be applied directly to powders, pills, and even to ointments. Destruction of organic matter, if necessary, can be conveniently effected by heating the material with sulphuric acid on the object-glass. The sublimed arsenious oxide crystallises in octahedra, tetrahedra, and, not infrequently, in monoclinic prisms. Should the crystals be small, addition of a little water or glycerol causes the formation of larger crystals. The sublimate should always be tested with silver nitrate; for this purpose, it is dissolved in warm water beneath the cover-glass; on one side of the latter a drop of 0·1% silver nitrate is added, and on the other side a drop of very dilute ammonia. A chrome-yellow precipitate, which slowly becomes brownish-yellow, is formed at the junction of the liquids.   H. W.

Silver-asbestos, Lead Chromate-asbestos and Lead Peroxide-asbestos. O. BINDER (*Chem. Zeit.*, 1918, **42**, 522).—A mixture of asbestos and finely divided metallic silver may be used for the absorption of chlorine in the combustion of organic substances; asbestos mixed with lead chromate or peroxide serves for the absorption of sulphur compounds. The silver is prepared by reducing ammoniacal silver nitrate solution with zinc. [See, further, *J. Soc. Chem. Ind.*, December.]   W. P. S.

Errors in Alkalimetry due to the Presence of Carbon Dioxide in Distilled Water. G. BRUHNS (*Zeitsch. anal. Chem.*, 1918, **57**, 257—277).—Attention is directed to the influence of dissolved carbon dioxide in water and in standard acid and alkali solutions on acidimetric and alkalimetric titrations. [See, further, *J. Soc. Chem. Ind.*, 730A.]   W. P. S.

The Iodotannic Reagent. D E. TSAKALOTOS and D. DALMAS (*Bull. Soc. chim.*, 1918, [iv], **23**, 391—400).—The reagent is a mixture of 1 c.c. of $N/10$-iodine solution with 1 c.c. of a 1% tannin solution, and is used to determine the alkalinity of very dilute alkaline solutions. The procedure is as follows. To the 2 c.c. of reagent in a porcelain dish, the alkaline solution is added with stirring until a definite red colour appears. From this point, the alkaline solution is run in gradually, and, after each addition, a drop of the mixture is tested on starch-paper. The end-point is reached when a blue colour is no longer formed on the test-paper. From a table given in the original, the alkalinity of the solution may then be calculated, knowing the volume of solution used. By means of this reagent exact results may be obtained with alkaline solutions at a dilution of $N/10,000$ to $N/40,000$.

W. G.

Simplification in the Estimation of Potassium. W. HÜTTNER (*Kali*, 1918, **12**, 178—179; from *Chem. Zentr.*, 1918, ii, 402—403).—The process depends on the substitution of barium bromide, $BaBr_2,2H_2O$, which is soluble in alcohol for the insoluble chloride. It is essential that the specimen of bromide should leave no residue when treated with alcohol; it is conveniently prepared from potassium bromide and barium carbonate, evaporation, and extraction of the residue with alcohol.

A weighed quantity of the potassium salt is dissolved in cold water, an excess of a highly concentrated aqueous solution of barium bromide is added, and the mixture is shaken and made up to the mark. The precipitate settles well; it is filtered, and 10 c.c. of the filtrate are treated with perchloric acid. Solution in cold water should be more generally adopted; specimens of carnallite, except as regards any kieserite, are immediately dissolved. The residue does not generally contain potassium. If this should be the case, the carnallite contains notable quantities of soluble potassium sulphates (polyhalite, langbeinite, etc.), and must be dissolved in the hot solvent. In this case, it is advisable to add hydrobromic instead of hydrochloric acid to prevent subsequent formation of barium chloride from the bromide. H. W.

Recovery of Silver from Albumose-silver Solutions and Methods for the Analysis of the latter. G. MAUE (*Chem. Zeit.*, 1918, **42**, 513—515).—Precipitation as chloride or thiocyanate in sulphuric acid solution is recommended for the recovery of silver from waste therapeutical albumose-silver solutions; the silver chloride or thiocyanate is subsequently collected, and fused with alkali carbonate and nitrate in order to obtain metallic silver. The most trustworthy methods for estimating the silver content of albumose-silver solutions are those based on the reduction of the silver by lactose or tannin in alkaline solution, or on its precipitation as bromide, iodide, chloride, thiocyanate, or ferrocyanide in acid solution. The precipitated silver or silver compound is

then fused with alkali carbonate and nitrate, the metallic silver dissolved in nitric acid, and titrated with thiocyanate solution. [See, further, *J. Soc. Chem. Ind.*, December.] W. P. S.

Estimation of Magnesium. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 211—212).—In the absence of large quantities of potassium chloride or sodium chloride, magnesium may be precipitated and weighed as $MgNH_4PO_4,6H_2O$. The precipitation is made at 90°, and the precipitate is collected after twenty-four hours, washed with ammonia and methyl alcohol, dried over calcium chloride, and weighed. [See, further, *J. Soc. Chem. Ind.*, 751A.] W. P. S.

Analysis of Magnesite. V. MACRI (*Boll. chim. farm.*, 1918, **47**, 301—302).—The volumetric method given by Merck Guano & Phosphat Werken (A., 1909, ii, 619) for analysing magnesite does not give trustworthy results. The author describes a modification of the usual method, by means of which risk of loss by projection during evaporation on a sand-bath is avoided. [See *J. Soc. Chem. Ind.*, December.] T. H. P.

Alkali Iodides as Reagents for Cadmium and Nickel. A. AGRESTINI (*Gazzetta*, 1918, **48**, ii, 30—34).—With a distinctly ammoniacal solution of a cadmium salt, 20—30% potassium iodide solution yields a heavy, white precipitate composed of regular octahedra and having the formula $Cd(NH_3)_2I_2$, whereas with a solution of a copper salt no precipitate forms under similar conditions. With the same reagent, strongly ammoniacal solutions of nickel salts give a heavy, bluish-violet precipitate of the formula $Ni(NH_3)_6I_2$, and consisting of microscopic, regular octahedra. Cobalt also gives a precipitate with this reagent, and must be removed before testing for nickel. [See *J. Soc. Chem. Ind.*, 751A.] T. H. P.

Volumetric Estimation of Lead in Tin Plate. J. DEININGER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 66—67).—The metal is dissolved in concentrated sulphuric acid, ammonium oxalate solution is added to complete the solution of the iron, and the lead sulphate is collected and dissolved in hot 50% sodium acetate solution. Bromine is added to precipitate the lead as peroxide, and this is then collected, dissolved in sodium acetate solution, and estimated iodometrically. [See, further, *J. Soc. Chem. Ind.*, 736A.] W. P. S.

Gravimetric Estimation of Copper by means of Sodium Nitroprusside and the Separation of Copper and Mercury. EMIL VOTOČEK and JAN PAZOUREK (*Chem. Zeit.*, 1918, **42**, 475—476).—The solution containing the copper salt is treated with an excess of sodium nitroprusside solution acidified previously with $N/10$-sulphuric acid, the mixture is diluted to 170 c.c., shaken for two to four hours, the precipitated cupric nitroprusside then collected on a tared filter, washed with water, dried at 110°, and weighed. The precipitate contains 22·75% of copper. This

method may be applied to the precipitation of copper in the presence of mercury salts provided that sodium chloride is also added to prevent precipitation of mercuric nitroprusside (compare this vol., ii, 238, 272). The mercury in the filtrate from the cupric nitroprusside may be estimated as sulphide or volumetrically, as described previously (*loc. cit.*). [See, further, *J. Soc. Chem. Ind.*, 751A.]   W. P. S.

Iodometric Estimation of Copper. I. M. KOLTHOFF (*Pharm. Weekblad*, 1918, **55**, 1338—1346).—A summary of the literature of the iodine method of estimating copper, and an account of the results obtained by varying the experimental conditions.
                                                                    A. J. W.

Gallium. L. M. DENNIS and J. ALLINGTON BRIDGMAN (*J. Amer. Chem. Soc.*, 1918, **40**, 1531—1561).—The spark spectra and arc spectra of gallium, indium, and zinc have been studied with the object of ascertaining the amounts of each of these elements which could be detected in the presence of large quantities of the other elements by this means. It is shown that 0.0046 mg. of gallium can be detected by means of the spark spectrum, the lines $\lambda = 4172$ and $4033\,\mu\mu$ being used for the purpose. In the case of indium, 0.0013 mg. may be detected by means of the spark lines $\lambda = 4511$ and $4102\,\mu\mu$. In the presence of gallium, quantities of indium as small as 0.06% of the weight of the gallium are detectable by the spark spectrum, whilst in the presence of indium, quantities of gallium amounting to 0.18% of the weight of the indium may be similarly detected.

It is shown that the fractional electrolysis of a dilute solution of indium and gallium sulphates is capable of yielding perfectly pure gallium after about fourteen electrolyses. Pure gallium chloride can be obtained from mixtures of gallium, indium, and zinc by the fractional distillation of the chloride in a current of chlorine.

The methods of estimation of gallium were studied, and it is shown that precipitation as hydroxide by means of ammonia leads to low results, because of the tendency of the precipitate to adhere to the beakers. Satisfactory results are obtained by precipitating gallium hydroxide from slightly acid solutions by means of sodium azide in boiling solution. Equally good results are obtained by precipitation of the hydroxide by adding sodium sulphite to the solution and boiling vigorously for four minutes. The last method has the advantage that physiologically active gases are not given off during the boiling, and so it is more agreeable to work with.

Zinc can be estimated in the presence of gallium by adding an excess of potassium mercuric thiocyanate to a slightly acid (H_2SO_4) solution of the sulphates. After keeping for several hours, the precipitate of zinc mercuric thiocyanate is filtered in a Gooch crucible and dried at 105—110°. The filtrate is acidified with hydrochloric acid and the mercury removed by

hydrogen sulphide, and, after boiling to expel the excess of hydrogen sulphide, the gallium is estimated as hydroxide by means of potassium sulphite.

Mixtures of gallium and indium are separated and estimated as follows. Solutions containing small amounts of both elements are largely diluted and treated with a small amount of hydrochloric acid, and then exactly neutralised with sodium hydroxide, an excess of 1·5 grams of sodium hydroxide is added, and the solution boiled for several minutes. The precipitated indium hydroxide is well washed, dissolved in hydrochloric acid, and the process repeated. Finally, it is dissolved again in hydrochloric acid, and precipitated by ammonia, washed, dried, ignited, and weighed as oxide. The filtrates and washings from each precipitation are combined, and the gallium precipitated as hydroxide by means of sodium sulphite, as described above.

The separation of gallium and aluminium is effected in the following way. The aluminium is precipitated as hydrated chloride by adding 60 c.c. of hydrochloric acid to the solution, and then 60 c.c. of ether. The flask is immersed in cold water and the solution saturated with hydrogen chloride, when hydrated aluminium chloride is precipitated. This is filtered on a Gooch crucible, washed with a mixture of 30 c.c. hydrochloric acid and 30 c.c. ether, and then dissolved in water, and the aluminium estimated as oxide in the usual way. The combined filtrates and washings are treated with a small amount of sulphuric acid and heated to expel the ether, and most of the hydrochloric acid and the gallium estimated as oxide after precipitation with sodium sulphite. Three methods of separating and estimating mixtures of gallium, indium, and zinc, and one method of estimating mixtures of gallium, indium, zinc, and aluminium, are described. For details of these, the original paper should be consulted.

Gallium selenate has been prepared by digesting gallium hydroxide in selenic acid solution at the boiling point for several hours. After filtration, minute, very soluble crystals were obtained which show oblique extinction. The air-dried salt has the formula $Ga_3(SeO_4)_3,16H_2O$, but there is evidence that the salt which separates from water solution at the ordinary temperature is $Ga_2(SeO_4)_4,22H_2O$. The air-dried salt dissolves in water to the extent of 1 part in 1·74 parts of water at 25°. Gallium cæsium selenate alum has been prepared by crystallising a mixture of the two salts. This substance dissolves in water to the extent of 1 part in 24·1 parts of water. The solubilities of ammonium gallium, and cæsium gallium sulphate alums have been determined in water, 50% alcohol, and 70% alcohol. The following solubilities were found : ammonium gallium alum, 1 part dissolves in 3·24 parts of water, 4600 parts of 50% alcohol, and 11,400 parts of 70% alcohol ; cæsium gallium alum, 1 part dissolves in 66·2 parts of water, 25,800 parts of 50% alcohol, and 28,000 parts of 70% alcohol. The solubility determinations were made at 25°.   J. F. S.

Magneto-chemistry. Applications to Analytical Chemistry. II. A. QUARTAROLI (*Gazzetta*, 1918, **48**, i, 65—78).— The method previously devised (A., 1916, ii, 123) for the estimation of magnetic salts in solution by measuring the magnetic susceptibility may be replaced by the procedure described below, which may be used with magnetic fields of moderate intensity and requires no special apparatus.   By means of truncated conical poles with circular faces, a field is obtained in which a zone of great intensity is separated sharply from one of feeble intensity. The solution to be examined is introduced into a small tube of about 8 mm. internal diameter, and above it is placed, carefully and without mixing, coloured water.   The tube is then arranged so that the surface of separation of the two liquids corresponds with the lower point where the poles begin to diverge.   When the magnet is excited, the water bulges out into the magnetic solution beneath without sensibly mixing with it, and if the field is sufficiently intense and the susceptibility of the solution great enough, a globule of the water becomes detached and remains suspended in the magnetic liquid.   The phenomenon is visible with weak fields and dilute solutions which yield scarcely perceptible indications by Plücker's or the U-tube method.   Naturally, the results become more marked as the specific gravities of the two liquids approach equality.

In the application of this phenomenon to quantitative analysis, a standard solution of ferric chloride containing a little hydrochloric acid is placed in the lower part of the tube, and the solution of the ferric salt to be analysed carefully pipetted on to the top of this solution; the upper liquid is then gradually diluted with successive diminishing quantities of water until only a just perceptible bulge slowly appears; the magnet should be excited for at least a minute, and the disappearance of the phenomenon when the current is interrupted employed as a control.   The results thus obtained with ferric chloride solutions of the respective concentrations 0·519, 0·2076, 0·0798, 0·0322, 0·0129, and 0·00515% were 0·5176, 0·2070, 0·0794, 0·0318, 0·0126, and 0·00500% with a field of 12,000 gauss, and 0·5181, 0·2073, 0·0795, 0·0320, 0·0127, and 0·00504% with a field of 30,000 gauss; in the latter case, a 0·002% solution gave the value 0·00184%.

As the magnetic susceptibility of ferric sulphate is, for certain concentrations, rather higher than that of the chloride, the sulphate ion should be removed by precipitation with barium chloride, followed by either filtration or decantation.   The actual determination then occupies usually about fifteen minutes, and at most 2 c.c. of the liquid are necessary.   The surface of separation is often visible owing to variation in the refraction, but it is convenient to add one of the ordinary indicators to the water used for dilution.

The determination of iron in this way is not affected by the presence in the solution of aluminium, phosphoric acid, etc., but if manganese or chromium salts are present, modification is necessary.

When, as is usually the case, the manganese is in small proportion, it may be determined colorimetrically and the percentage found subtracted directly from the percentage of iron found by the magnetic method, the atomic weights of the two elements and the susceptibilities of their salts differing only slightly. With marked quantities of manganese, the latter should be converted into permanganic acid, which is virtually non-magnetic; the manganese is thus determinable from the difference of the susceptibilities before and after this transformation; also, when chromium is present, this is converted into chromate, which is negligibly magnetic.

The optimum concentrations for the chromium, manganese, nickel, and cobalt solutions to be used are given, and the application of the method described to (1) volumetric analysis with permanganate, (2) volumetric analysis with dichromate, and the analysis of mixtures of chromic salts and chromates, (3) the analysis of solutions containing ferrocyanides, ferricyanides, thiocyanates, and organic matter.   T. H. P.

Influence of Iron and Organic Matter on the Iodometric Estimation of Chromium. R. LAUFFMANN (*Ledertechn. Rundsch.*, 1918, **10**, 37—39; from *Chem. Zentr.*, 1918, ii, 310—311).—If oxidation is effected with sodium peroxide, the results are high in the presence of notable quantities of iron, in consequence of increased separation of iodine; when considerable amounts of hydroxides or silica are formed during fusion or subsequent acidification and are removed by filtration, the results are low, owing to adsorption of chromium. If the precipitate consists of bases which do not cause the separation of iodine and are soluble in hydrochloric acid, it is dissolved in this reagent, and the chromium is estimated in the solution. Large amounts of organic matter cause inexact results when the oxidation is effected with sodium peroxide, since, unless completely destroyed, they give rise to substances which delay the separation of iodine and cause the end-point of the titration to be indefinite. In the presence of considerable quantities of iron or organic matter, oxidation is conveniently effected with a mixture of sodium carbonate (120 parts), potassium carbonate (40 parts), and potassium chlorate (8 parts), or, in absence of organic matter, by treatment with Mohr's salt (compare Schorlemmer, this vol., ii, 372). In presence of organic matter, oxidation may be achieved with potassium permanganate (compare Schorlemmer, *loc. cit.*), and the chromium may be estimated in the filtrate.   H. W.

Analysis of Molybdenum Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour. PAUL JANNASCH and OTTO LAUBI (*J. pr. Chem.*, 1918, [ii], **97**, 154—181).—The molybdenum compound is heated at 400° to 560° in a current of carbon tetrachloride vapour; the molybdic acid volatilises, and is collected in a receiver, evaporated with nitric acid, ignited, and weighed. The method is generally applicable to molybdates and

ores, and may be used for the analysis of ferromolybdenum and molybdenum silicide; in the case of the last two compounds, silicon and iron also volatilise, and are separated subsequently from the molybdic acid. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

Analysis of Tungsten Compounds by Volatilisation in a Current of Carbon Tetrachloride Vapour. PAUL JANNASCH and ROBERT LEISTE (*J. pr. Chem.*, 1918, [ii], **97**, 141—153).— Tungstic acid is readily volatilised when heated in a current of carbon dioxide saturated with carbon tetrachloride vapour. The volatilised substance is collected in a receiver, and subsequently evaporated with nitric acid, ignited, and weighed. The method may be applied to the estimation of tungsten in ammonium tungstate, sodium tungstate, calcium tungstate, lead tungstate, scheelite, wolframite, etc. [See, further, *J. Soc. Chem. Ind.*, 732A.]

W. P. S.

A Method for the Rapid Analysis of Mixtures of Chlorinated Toluene. HERBERT A. LUBS and ARTHUR B. CLARK (*J. Amer. Chem. Soc.*, 1918, **40**, 1449—1453).—The sample (about 0·5 gram) is placed in a sealed tube with water (10 c.c.) and briskly shaken in a bath of boiling water for two hours; the contents of the tube are washed into a small assay flask, and the tube is rinsed out with water (free from carbon dioxide) and with alcohol if any benzoic acid remains. The solution is then titrated with alkali in the presence of thymolsulphophthalein according to the authors' method (this vol., ii, 449). The percentage of benzotrichloride (x) is calculated from the benzoic acid formed; the percentages of benzylidene chloride (y) and benzyl chloride (z) are derived from the following relations: $x + y + z = 100$; $0·545x + 0·434y + 0·281z =$ per cent. side-chain chlorine. The method is very suitable for plant control work, and, if certain precautions are taken (*loc. cit.*), will give a high degree of accuracy.

H. W.

New Method of Determining the Amount of Methyl Alcohol in Mixtures of Ethyl and Methyl Alcohols. WILLIAM G. TOPLIS (*Amer. J. Pharm.*, 1918, **90**, 636—640).—The method is designed principally for the rapid testing of denatured spirits, and is based on the measurement of the volume of hydrogen evolved by sodium from the alcohol previously dehydrated by treatment with fused potassium carbonate. The determination is carried out by comparison with a sample of denatured alcohol of known composition, so that a correction for temperature and pressure of the gas is not necessary. The sodium on the end of a needle is suspended by a thread passing through the gas-leading tube. The reaction is carried out in a test-tube, to which six drops of the alcohol to be tested are added. The gas is evolved when the thread is released, after bringing the gas-delivery orifice under an inverted burette filled with light petroleum and sup-

ported in a hydrometer jar containing the same liquid. [See, further, *J. Soc. Chem. Ind.*, 711A.] J. F. B.

Colorimetric Estimation of Phenols in the Blood. STANLEY R. BENEDICT and RUTH C. THEIS (*J. Biol. Chem.*, 1918, **36**, 95—98).—The method consists in removing the proteins by boiling with dilute acid and alumina cream, and then estimating the total phenol + uric acid by a modification of the method of Folin and Denis (A., 1912, ii, 1011), using the phosphotungstic–phosphomolybdic reagent, excess of sodium carbonate, and, in addition, sodium hydrogen sulphite, which has a marked clarifying action. The colour is compared with that obtained from a standard resorcinol solution (0·581 mg. in 5 c.c., equivalent to 0·5 mg. of phenol in 5 c.c.), which may be preserved unchanged for several months. The uric acid is then estimated in another sample of the blood, and the difference gives the required content of phenol in the blood. H. W. B.

Colorimetric Estimation of Cholesterol in Blood ; Estimation of Coprosterol in Fæces. VICTOR C. MYERS and EMMA L. WARDELL (*J. Biol. Chem.*, 1918, **36**, 147—156).—One c.c. of the blood, plasma, or serum is mixed with plaster of Paris and, after drying, directly extracted with chloroform. The extract containing the cholesterol is treated with acetic anhydride and concentrated sulphuric acid, and the colour which develops is compared with a standardised aqueous solution of naphthol-green B.

For the estimation of coprosterol, the fæces are treated with calcium and sodium hydroxides to saponify fats and remove bile pigments, and the residue is mixed with plaster of Paris and extracted with chloroform, as indicated for the estimation of cholesterol in the blood. Normal human blood contains from 0·100 to 0·164% of cholesterol. H. W. B.

Estimation of Aldose Sugars by means of Iodine in Alkaline Solution. Applications. H. COLIN and O. LIÉVIN (*Bull. Soc. chim.*, 1918, [iv], **23**, 403—405).—A slight modification of Bougault's method (compare A., 1917, ii, 395), the alkaline solution used containing 35 grams of sodium phosphate and 50 c.c. of *N*-sodium hydroxide per litre. An $N/10$-solution of iodine is used, and considerable excess added, the volume of alkaline solution used being double that of the iodine solution. The reaction is complete after one hour, and the excess of iodine is titrated back after making the solution just acid with sulphuric acid. Satisfactory results were obtained with the roots or tubercles of artichokes and chicory. W. G.

[Estimation] of Formic Acid, Acetic Acid, and Lactic Acid [in Admixtures]. ISENOSUKE ONODERA (*Ber. Ohara Inst. landw. Forsch.*, 1917, **1**, 231—269).—The three acids are extracted with ether from their aqueous solution ; a portion of the extract is

oxidised with permanganate in alkaline (sodium carbonate) solution, and the excess of permanganate then titrated. This gives the formic acid and lactic acid together. Another portion of the extract is oxidised with permanganate, and the oxalic acid resulting from the oxidation of the lactic acid is precipitated as calcium oxalate and estimated volumetrically. Acetic acid is estimated by extracting a third portion with ether, diluting the extracted acid to 100 c.c., and distilling the solution until 95 c.c. of distillate have been collected; under these conditions, the distillate will contain 84·49% of the acetic acid. [See, further, *J. Soc. Chem. Ind.*, 715A.]   W. P. S.

New Method for the Accurate Estimation of the Content of Fatty Acids in Soaps. E. BOSSHARD and F. COMTE (*Helv. Chim. Acta*, 1918, **1**, 251—270).—Errors are introduced in the estimation of the fatty acids in soaps when these are weighed as such, owing partly to the oxidation of the unsaturated acids and partly to the volatility of the lower fatty acids. The authors describe a method in which the acids are weighed in the form of the lead salts. An ethereal solution of the acids is evaporated in contact with lead oxide, the increase in weight thus representing the weight of the acid anhydrides. [See *J. Soc. Chem. Ind.*, 707A.]   C. S.

Biochemical Colour Tests. I. Thiophen Test for Lactic Acid. A Colour Test for Aldehydes. WILLIAM ROBERT FEARON (*Biochem. J.*, 1918, **12**, 179—183).—The thiophen reaction for lactic acid is due to the production of formaldehyde and, chiefly, acetaldehyde from the lactic acid, which interact with the thiophen in the presence of excess of sulphuric acid to give the cherry-red colour. Acetaldehyde is much less stable in dilute than in 'strong sulphuric acid, and consequently if there is more than a trace of water present at the outset, the acetaldehyde will be destroyed as it is produced, and the thiophen will give no coloration.

The following general test is described for the detection of aldehydes. A couple of drops of a 0·2% alcoholic solution of thiophen are added to 5 c.c. of concentrated sulphuric acid (free from nitrites and nitrates) and mixed. On adding a drop of a weak solution of an aldehyde, a red colour develops and spreads through the acid. The test is sufficiently delicate to detect 1 part of formaldehyde in 100,000. The colour varies slightly with different aldehydes; substituted aldehydes, such as chloral, *p*-hydroxybenzaldehyde, etc., also give the test. The colours produced by this test are all discharged by a few drops of water, but are reproduced on the addition of more sulphuric acid. The author suggests the term " hydrocnic " to describe this and similar tests in which the colour produced is unstable towards water.

On the addition of phosphoric oxide to a mixture of thiophen and acetaldehyde in light petroleum, interaction occurs, and one of the products is an orange *liquid*, b. p. 121° (decomp.), which may be dithienylmethylmethane, $CH_3 \cdot CH(C_4H_3S)_2$.   H. W. B.

Crismer Test for the Detection of Foreign Fat in Butter, Lard, etc. ALAN W. STEWART (*J. State Med.*, 1918, **26,** 312—315).—The following modification of Crismer's test (A., 1896, ii, 506) gives values for different fats which appear to be sufficiently distinctive to render the application of the test of value for the detection of adulteration in butter, lard, etc. Three c.c. each of filtered fat and absolute alcohol are pipetted into a test-tube and heated over a small flame until the mixture, which is continuously stirred with a thermometer, has become clear. The tube is then removed from the flame, and the contents stirred until turbidity reappears. The temperature at which this occurs constitutes the Crismer number. Butter-fat gives a result varying from 50·5 to 57, whilst margarine has a value above 65 if it is composed of animal fat and under 50 if prepared from vegetable fat. The fat must be free from moisture and quite clear, and can generally be so obtained by filtration through a dried filter-paper at 100°. The Crismer values of other fats and oils are as follows: lard, 76 to 77; sesame oil, 67·5; almond oil, 64; cotton-seed oil, 61·5; arachis oil, 57·5; olive oil, 56; cocoa butter, 47; tallow, 34·5; palm oil, 22; cocoanut oil, 15 to 19·5; palm kernel oil, 13·5. Rape oil is insoluble at the boiling point of the mixture with alcohol.

H. W. B.

New Method of Estimating Phosphatides. C. CIACCIO (*Arch. farm. sper. sci. aff.*, 1917, **24,** 231—234; from *Physiol. Abstr.*, 1918, **3,** 309).—The methods of estimation are given in full, and from the results the "phosphatide index," which is the ratio of fatty acids to lipoid phosphorus, is calculated. The index is lessened in certain pathological states, indicating partial cleavage of the lipoids.

H. W. B.

The Use of Benzaldehyde Sulphite Compounds as a Standard in the Quantitative Separation and Estimation of Benzaldehyde and Benzoic Acid. G. A. GEIGER (*J. Amer. Chem. Soc.*, 1918, **40,** 1453—1456).—The work was originally commenced with a view to the analysis of toluenes chlorinated in the side-chain based on an estimation of benzaldehyde and benzoic acid. The procedure is quite accurate and useful for control analyses, but inferior in point of speed and ease of manipulation to the method of Lubs and Clark (this vol., ii, 460). In the pre-liminary work, benzaldehyde was found to be unsuitable as a standard, as it is too readily oxidised, but the bisulphite compound, $PhCHO,NaHSO_3,\frac{1}{2}H_2O$, fulfils the required conditions.

The estimation is carried out as follows. Solutions containing as a maximum 0·5 gram of benzaldehyde and benzoic acid are made distinctly alkaline with sodium hydroxide and extracted with three portions of ether (each 25 c.c.); the combined ethereal extracts are treated with freshly distilled phenylhydrazine (1·5 gram) and 10 c.c. of a solution of acetic acid in ether (10%). The solution is evaporated in a current of air, the residue mixed with

water (50 c.c.), and the insoluble benzylidenephenylhydrazone collected in a tared Gooch crucible, dried for two hours at 70° in a vacuum, and weighed.

The solution from which the benzaldehyde has been extracted is rendered slightly acid with hydrochloric acid (1:3), extracted with chloroform (25 c.c.), saturated with salt, and three times extracted with chloroform (25 c.c. for each extraction). The chloroform is removed at the ordinary temperature, and the residue dissolved in neutral 50% alcohol and titrated with sodium hydroxide.

If the ethereal solution of benzaldehyde is washed with 25 c.c. of 0·2N-sodium hydroxide, the quantity of benzoic acid separated is larger and the accuracy of the method is increased. H. W.

Estimation of Acetone in Smokeless Powders. A. Pieroni (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 52—57).—A method is described by means of which the losses attending the conversion of acetone into iodoform and the estimation of the latter are avoided. [See *J. Soc. Chem. Ind.*, 749A.] T. H. P.

Estimation of Acetone in Urine. Sabel (*Rep. pharm.; Giorn. farm. chim.*, 1917, **66**, 27; from *Physiol. Abstr.*, 1918, **3**, 327).—Tartaric acid is added to 200 c.c. of urine, which are then subjected to distillation. To •50 c.c. of the distillate, a solution of iodine in potassium iodide is added, and then a slight excess of potassium hydroxide. The precipitated methyl iodide is washed with water and then heated under a reflux condenser with fuming nitric acid and silver nitrate. The silver iodide thus formed is washed, dried, and weighed. The weight multiplied by 0·1171 gives the amount of acetone. H. W. B.

New Volumetric Method for the Estimation of Uric Acid in Blood. L. J. Curtman and A. Lehrmann (*J. Biol. Chem.*, 1918, **36**, 157—170).—The proteins in the blood are coagulated by heat in the presence of dilute acetic acid, and, after filtration, the uric acid in the filtrate is precipitated by the addition of nickel acetate in the presence of sodium carbonate. The uric acid in the precipitate is subsequently estimated by adding an excess of standard iodine solution and titrating the excess with thiosulphate solution, using starch as indicator. H. W. B.

Estimation of the Purine Bases in Nucleic Acids after Cleavage without the Production of Humin. R. Feulgen (*Zeitsch. physiol. Chem.*, 1918, **102**, 244—251).—The nucleic acid is heated with a solution of sodium hydrogen sulphite at 160° under pressure, whereby a colourless, humin-free hydrolysate is obtained. On cooling, the guanine separates quantitatively, whilst the adenine in the filtrate is precipitated as phosphotungstate, then converted into the silver sulphate compound, and finally weighed as picrate. H. W. B.

Identification of Purine Bases in Drugs. O. Tunmann (*Pharm. Post.*, 1918, **51**, 305—306; from *Chem. Zentr.*, 1918, ii, 219—220).—Of the three known processes, sublimation on an asbestos plate and detection with gold chloride (if concentrated hydrochloric acid and gold chloride solution [3%] are added) yield trustworthy results; the benzene process is less satisfactory. A new method, in no way inferior to the gold chloride process, depends on the use of ammonia and chloroform. The section or powder is moistened with ammonia (this causes a strong green coloration with raw coffee), covered, treated with chloroform, and the liquids are mixed by inclining the slip. Separation of crystalline purine bases occurs within a few seconds with coffee, kola, and tea, more slowly with theobroma, and still more slowly (after about five minutes) with *Paullinia cupana*. The colourless needles either lie singly or are grouped in bundles.

Sublimation does not affect the free purine bases only, but the combined bases are also decomposed and the purine sublimes.

The ammonia–chloroform process only permits an approximate localisation of the bases. H. W.

Application of Microchemical Methods to the Investigation of Drugs. III. Acetoanilide, Acetphenetidide, Antipyrine, Amidopyrine (Pyramidone). Adolf Mayrhofer (*Zeitsch. Allg. Österr. Apoth. Ver.*, 1918, **56**, 39—41, 47—48, 57—60; from *Chem. Zentr.*, 1918, i, 1196—1197).—The microchemical recognition of acetanilide, phenacetin, and antipyrine has been described recently by Tunmann (A., 1917, ii, 551). Acetanilide may be detected by the melting point, crystalline form of aniline sulphate, and recognition of the acetyl group by ferric chloride. Identification of acetophenetidide depends chiefly on the reaction with nitric acid, the m. p., the crystalline form, and the sublimation. Antipyrine may be identified by m. p., sublimation, the *iso*nitrosoantipyrine reaction, the ferripyrine reaction, and by Wasicky's method with *p*-dimethylaminobenzaldehyde (this method is suitable for the detection of antipyrine as an impurity in other drugs); the latter test is conveniently performed by warming antipyrine with *p*-dimethylaminobenzaldehyde, when a deep yellow solution is formed, which becomes red after addition of a drop of water.

Pyramidone sublimes undecomposed slightly above its melting point, generally in droplets, which become crystalline when rubbed; the crystals appear as rectangular or quadratic plates or as rectangular needles generally united in clusters or twin crystals. The mercury double salt crystallises in needles or quadratic plates; it separates from alcohol in needles grouped in rosettes, to which slender, dendritic, crystalline threads are frequently attached. The potassium iodide–iodine reaction is much more sensitive; the yellow crystals obtained in dilute sulphuric acid solution dissolve when warmed and separate again on cooling as yellowish-brown, rectangular needles, sometimes pointed, frequently united to form aggregates. The reactions with hydriodic acid, zinc chloroiodide,

and potassium mercury iodide are also very sensitive. Silico-tungstic acid, after vigorous boiling in hydrochloric acid solution, yields regular, six-sided, almost colourless crystals; with antipyrine it gives only droplets, and does not react with acetanilide or phenacetin. Picric acid causes the separation of groups of yellow needles from a solution of pyramidone in hydrochloric acid.

H. W.

Volumetric Estimation of Histidine and other Glyoxaline Derivatives. C. L. LAUTENSCHLÄGER (*Zeitsch. physiol. Chem.*, 1918, **102**, 226—243).—Histidine can be estimated quantitatively by treating its solution with an excess of diazobenzenesulphonic acid, boiling with alcohol to destroy the excess of the acid, and then titrating the stable histidine dye with titanium trichloride by Knecht and Hibbert's method (A., 1903, ii, 509). An altern-ative method consists in adding standard silver nitrate to the histidine solution until a drop no longer gives a red coloration with an alkaline solution of diazobenzenesulphonic acid. As only the free base reacts with the diazo-acid to form a red dye, whilst the silver salt gives no colour reaction, the end-point is revealed by the non-appearance of the red coloration.

For its estimation in protein, the histidine must first be separated from the other products of hydrolysis, especially tyrosine, and this can be effected by means of silver lactate or mercuric chloride, which form insoluble compounds with histidine. H. W. B.

The Berberine Nitrate Test with Hydrastis Powder. OTTO ESS (*Schweiz. Apoth. Zeit.*, **56**, 104—105; from *Chem. Zentr.*, 1918, ii, 226).—The microchemical detection of berberine in hydrastis powder is best effected in the following manner: the powder is rubbed with a drop of alcohol and treated with two drops of nitric acid (30%); after a short time, yellow needles of berberine nitrate, up to $60\,\mu$ in length, and generally united in clusters, separate. The needles disappear when warmed, and the solution becomes red. H. W.

Differentiation between Egg-albumin and Pathological Albuminoids. C. PAGEL (*Bull. Sci. Pharmacol.*, 1918, **25**, 117—118; from *Chem. Zentr.*, 1918, ii, 76).—The following methods are considered trustworthy: (1) Salkowski's reaction. Nitric acid (D 1·2) is added drop by drop to the cold urine until a permanent turbidity or precipitate is obtained, followed by an equal volume of alcohol (95%); in the presence of urine-albumin, complete solution occurs, whilst with egg-albumin the turbidity is increased or a precipitate formed; in the course of twelve to twenty-four hours a considerable evolution of gas occurs in certain circumstances. (2) The urine is shaken with an equal volume of a mixture of ether (4 parts) and alcohol (95%, 1 part); in the presence of urine-albumin, a thin skin is at most formed between the layers, whilst with egg-albumin a thick layer filled with bubbles of air, which only slowly subsides, is produced; the aqueous-

alcoholic layer is cloudy and yields a precipitate within twenty-four hours. (3) A mixture of urine (10 c.c.) and alcohol (95%, 100 c.c.) is filtered after half an hour, and the filter-paper is pierced; urine-albumins dissolve in a few c.c. of water, whereas egg-albumin in quantities above 2 grams per litre remains undissolved. H. W.

Detection of Egg-albumin in Urine. C. BARBE (*Bull. Sci. Pharmacol.*, 1918, **25**, 118—121; from *Chem. Zentr.*, 1918, ii, 75). —Three to four c.c. of a mixture of 30 c.c. of ammoniacal copper oxide solution (prepared by repeatedly pouring 100 c.c. of officinal ammonia solution over about 1 gram of copper) diluted with acetic acid to 100 c.c. are cautiously introduced beneath 3—4 c.c. of clear, fresh urine in a test-tube. In the presence of egg-albumin, a more or less transparent, sharply defined ring is formed at the junction of the layers; with quantities of less than 0·10 gram per litre, reaction occurs within three minutes. H. W.

The Simulation of Albuminuria (Detection of Egg-albumin). ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1918, [vii], **18**, 201—204).—For the rapid and exact detection of egg-albumin in urine, a slight modification of Maurel's reagent is advised. The new reagent is prepared by mixing together 25 c.c. of 33% aqueous sodium hydroxide, 5 c.c. of 10% copper sulphate solution, and 70 c.c. of glacial acetic acid. With this reagent, a ring is formed at the surface of contact of the two liquids in 30 seconds, as compared with 75 seconds with Maurel's reagent, 150 seconds if the copper sulphate is not added, and 1200 seconds with acetic acid alone. W. G.

Preparation of Teichmann's Hæmin Crystals. N. BOKARIUS (*Vierthjschr. ger. Med. öffentl. Sanitätswesen*, 1918, [iii], **55**, 255—259; from *Chem. Zentr.*, 1918, ii, 121—122).—The most suitable reagent is a mixture of acetic acid (100%, 3 parts) and saturated common salt solution (0·3 part). The suspected stains are moistened with three or four drops of the reagent, and the liquid is pressed on to an object-glass; the preparation is covered and evaporated or boiled. Alternatively, a small quantity of the suspected substance is scraped on to an object-glass and moistened with three or four drops of the reagent, the subsequent procedure being the same as that described above. Special precautions need not be observed during the heating. H. W.

Analyses of Blood-gases. I. Qualitative and Quantitative Detection of Acids in Small Quantities of Blood by Estimation and Distribution Equilibria. H. STRAUB and KLOTHILDE MEIER (*Biochem. Zeitsch.*, 1918, **89**, 156—177).— The laws of mass action regulate the relationship between (*a*) the undissociated, (*b*) the dissociated parts of electrolytes in the blood, and (*c*) the hydrion concentration. If two of these are known, the third can be calculated. A method is described for determining whether acids stronger or near the strength of carbon dioxide

are present which depends on the solubility of carbon dioxide in blood or serum. It consists in the determination of the equilibria of distribution between carbon dioxide and the non-volatile acids of the blood. The determination of the absolute solubility of carbon dioxide at a given partial pressure of the gas, or at a given hydrion concentration, gives a means of estimating the amount of pathological acids present in blood. Various examples of the use of the method are given.   S. B. S.

Estimation and Meaning of Ferments in Gastric Juice. L. MICHAELIS (*Deutsch. med. Woch.*, 1918, **44**, 685—689; from *Chem. Zentr.*, 1918, ii, 288—289).—The communication deals with rennet and pepsin. In the estimation of the former, the action of gastric juice on milk is compared with that of a standard solution of rennet prepared from a known, stable rennet preparation, such as Merck's rennet tablets. The interpretation of varying concentrations of rennet and hydrochloric acid in the gastric juice is discussed.

The estimation of pepsin depends on the fact that certain solutions of albumin which become cloudy on addition of sulphosalicylic acid are smoothly fermented by pepsin in the presence of this acid; all other precipitants of albumins destroy the action of pepsin. For the estimation, as in that of rennet, a control ferment is required; a stable pepsin solution is used for this purpose, which is standardised by comparison with a series of normal gastric juices containing, as a mean, fifteen pepsin units. The albumin solution is best prepared from a strongly albuminous urine, which is preserved by chloroform, and so diluted that it contains about 0·5% of albumin. Sulphosalicylic acid (10%) is added to this until the solution is just distinctly acid to Congopaper, but only gives a faint violet colour. After remaining for a few minutes in a test-tube, the solution should show a just non-translucent turbidity. All the solutions must have the same hydrogen-ion concentration, which is attained in practice by using an excess of the albumin–acid solution in comparison with the amount of gastric juice, so that the influence of the latter on the action of the mixture is negligible. For the estimation, six tubes are charged with 1 c.c. of gastric juice, the latter being used pure and in dilutions of 1/2, 1/4, 1/8, 1/16, and 1/32 respectively. A control tube containing 1 c.c. of pepsin solution (1 pepsin unit) is also used. Five c.c. of albumin–acid solution are added to each tube, and the series is placed in a thermostat at 37°. After about ten minutes, a certain degree of clarification is observed in the control tube, and the solutions in the other tubes are now compared with it.

The detailed experiments show a certain parallelism between acidity, rennet, and pepsin; the relationship is only approximate, however.   H. W.

INDEX TO PATENTS.

ERRATA.

Vol. LXXXII (Abstr., 1902).

Part I.

Page Line
174 22   and throughout the abstract, *for* "tropic" *read* "tropinic."

Part II (Index).

Page Line
743 7* col. i. }
1032 27 ,, i. } *for* "tropic acids," *read* "tropinic acids."

Vol. XCIV (Abstr., 1908).

Page Line
ii. 395 22* *for* "$C_{15}H_{20}O_6Ag$" *read* "$C_{15}H_{20}O_6Ag_2$."

Vol. C (Abstr., 1911).

Page Line
ii. 406 18 *for* "durites" *read* "dunites."
ii. 1105 7* ,, "1910, A., ii, 57" *read* "1910, A., ii, 46."

Vol. CII (Abstr., 1912).

Page Line
ii. 57 19 *for* "idiocrase" *read* "idocrase."
ii. 173 2 ,, "rhodocrosite" *read* "rhodochrosite."
ii. 357 14 ,, "sopal" *read* "opal" ?
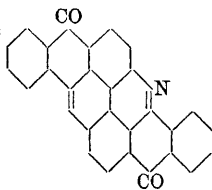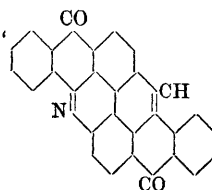
Vol. CIV (Abstr., 1913).

Page Line
ii. 419 14 *for* "Rev. . . ." *read* "Riv. Min. Crist. Ital."
ii. 419 20* ,, "samseyite" *read* "semseyite."
ii. 423 3 ,, "hornblende" *read* "hornfels."
ii. 423 7 ,, ' double refraction (mean value 1·67)" *read* "mean index of refraction 1·67."

Vol. CXII (Abstr., 1917).

Page Line
i. 660 22* *for* "**Bixins**" *read* "**Bixin. IV.**"
i. 660 21* ,, "425" *read* "495."
i. 683 7* ,, "**89**" *read* "**39.**"
ii. 112 7 ,, "nitrate" *read* "nitrite."
ii. 457 2 ,, "Genossen" *read* "collaborators."
ii. 496 18* ,, "hedenbergit" *read* "hedenbergite."

Vol. CXIV. (Abstr., 1918).

Page Line
i. 275 15 *for* "Fridricia" *read* "Fridericia."
i. 282 25 ,, "Galbransen" *read* "Gulbransen."

i. 307 10 ,, "   " *read* "   "

* From bottom.

647

Page	Line	
i. 342	15*	*for* "*p*-**Aminophenol**" *read* "**Nitrobenzene**."
i. 343	25	,, "benzoyl" *read* "benzyl."
ii. 17	9	,, "Wengel" *read* "Wenzel."
ii. 21	6*	*Insert* "[Compare, however, Fenton, Trans., 1894, **65**, 899]."
ii. 63	15*	*for* "flame" *read* "plane."
ii. 69	4	*after* "2 : 4-dinitrotoluene" *insert* "the system."
ii. 69	4*	*for* "molecudes" *read* "molecules."
ii. 95	8	,, "ZACHS" *read* "LACHS."
ii. 102	15* / 14*	*delete* "[See *Ind.*, 71A]."
ii. 120	4*	*for* "2CaO, VO₃, 3CO₂, 1OH₂O" *read* "2CaO, VO₂, 4CO₂, 1OH₂O."
ii. 323	10 / 15	,, "**Sulpharsenate**" *read* "**Sulpharsenite**." / ,, "5%" *read* "25%."
ii. 326	12*	,, "**Vasca**" *read* "**Vaca**."
ii. 372	23	,, "Tancey" *read* "Yancey."
ii. 470	10	col. ii. *for* "i, 279" *read* "ii, 279."

COLLECTIVE INDEX, 1893—1902 (AUTHORS)

Page	Col.	Line	
218	i	18*	*for* "tropic acids," *read* "tropinic acids."
1641	ii	3 & 4	*delete.*
1642	i	23*	*insert* "**Tropinic Acids** (GADAMER) 1902, A., i, 174."

COLLECTIVE INDEX, 1903—1912 (AUTHORS).

Page	Col.	Line	
886	i	22	for "*Butea fundosa*" read "*Butea frondosa.*"
1012	i	9*	*for* "1904, A., i, 24" *read* "1904, A., ii, 39."

SUBJECTS.

Page	Col.	Line	
278	i	20	*for* "A., ii, 868" *read* "A., i, 868."
1317	ii	23* and 24*	should be deleted.
1326	ii	30*	below this line *insert* "**3-Methoxy-4-toluic acid**, methyl ester" (GUILLAUMIN), 1910, A., i, 375.

NOTE TO T., 1917, **111**, 664—665.

The word "pure" in this section is intended to convey that the zinc sulphide in question was free from any intentional impurities, and that, so far as could be provided, it was also free from quantities of impurity detectable by ordinary chemical methods. It was not intended to suggest that the sulphide was spectroscopically pure. The methods of preparation described in the section obviously cannot provide against the contamination of the product with traces of zinc oxide.

* From bottom.